Journal of Materials Chemistry C

PAPER

Cite this: J. Mater. Chem. C, 2013, 1, 4885

Received 12th April 2013 Accepted 16th June 2013 DOI: 10.1039/c3tc30681j

www.rsc.org/MaterialsC

1 Introduction

Photoelectronic metal-containing polymers have attracted enormous attention because they have extensive applications in polymeric light-emitting diodes (PLEDs),¹ memory devices,² polymer solar cells,³ and so on. It is believed that electroluminescent (EL) polymers are superior in low-cost and large-area display device fabrication because of their solution processability.⁴ However, as fluorescent emitters and mixtures with polydisperse molecules, EL polymers have the common disadvantages of low EL efficiency and poor color purity, and these poor properties remarkably restrain their applications in high

Efficient monochromatic red-light-emitting PLEDs based on a series of nonconjugated Eu-polymers containing a neutral terpyridyl ligand[†]

Chaolong Yang,^{abc} Jing Xu,^{ac} Yunfei Zhang,^{ac} Yinwen Li,^{ac} Jian Zheng,^{ac} Liyan Liang^a and Mangeng Lu^{*a}

Three novel Eu-polymers containing hole transporting units and light-emitting units in the main chain have been designed and synthesized via radical copolymerization of N-vinylcarbazole and polymerizable Eu(TTA)₃vinyl-tpy, where TTA is 2-thenoyltrifluoroacetonate. The chemical structure and composition of the Eu-polymers were characterized by FTIR, UV-vis, ¹H NMR, ¹³C NMR spectroscopy, GPC, ESI-MS, and elemental analysis. The geometry of the polymerizable monomer Eu(TTA)₃vinyl-tpy was predicted using the Sparkle/PM6 model and suggested to be in a chemical environment with very low symmetry around the Eu³⁺ ions (C₁), in agreement with the fluorescence spectrum. All Eu-polymers exhibited good solubility, as well as good thermal stability and high glass transition temperatures. The photoluminescence (PL) properties of the copolymers in solution and in the solid state were investigated in detail. Intramolecular energy transfer from the carbazole groups to the europium complexes occurred even in diluted solutions. The efficiency of this process also depended on the composition of the Eu-polymers. In the solid state, emission from the carbazole groups was suppressed and the absorbed excitation energy was transferred effectively to the europium complexes in the Eu-polymers. Most importantly, the EL performances of eight pure red-emission PLEDs based on P1, P2, and P3 as the emitting layer have been studied in detail. Bright electroluminescence with a maximum luminance of 68.2 cd m^{-2} from the double-layer devices of P1 was demonstrated. Although the EL performance was only the third-best among those of the Eu-chelated polymers reported so far, to the best of our knowledge, this is the first example of electroluminescent devices of Eu-polymers based on tpy as a neutral ligand. These results illustrate the potential application of polymerizable tpy ligands in high performance EL Eu-chelated polymers.

> performance displays, such as for high contrast ratios. In fact, for some special applications, such as photosignal identification and processing, the color purity is as important as the emission intensity. A number of reported results indicate that small molecular electro-phosphorescent dyes, such as transition-metal complex units have been introduced into the main chains or side chains of polymers to construct electro-phosphorescent polymers, which can efficiently improve the EL efficiencies.⁵

> However, the full widths at half maximum (FWHM) of these polymers were still around 100 nm, which becomes a main constraint for their application in high color purity display devices. As is commonly known, lanthanide complexes, especially Eu- and Tb-complexes, have excellent color purity.⁶ To date, a number of organic Eu-complex luminescent materials have been extensively studied as one kind of the most important red-emitting materials in organic light-emitting diodes (OLEDs) because of their pure red monochromic characteristic emission with FWHM of 5–10 nm, high photoluminescent (PL) efficiency, chemical environment stability and theoretical internal quantum efficiency approaching 100%.⁷

RSCPublishing

View Article Online

^aKey Laboratory of Polymer Materials for Electronics, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, P.R. China. E-mail: mglu@gic.ac.cn

^bSchool of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400054, P.R. China. E-mail: yclzjun@163.com

^cUniversity of Chinese Academy of Sciences, Beijing 100039, P.R. China. E-mail: mglu@gic.ac.cn

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c3tc30681j

To further improve the EL efficiencies of Eu-complexes, many bright and efficient electroluminescent devices based on small molecular Eu-complexes are achieved through doping/ blending, in which 4,4'-N,N'-dicarbazolebiphenyl (CBP),8 2-biphenyl-4-yl-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD),⁹ and polyvinylcarbazole (PVK)¹⁰ with high triplet excited energy levels are often used as the hosts. Though such doped devices have the advantage of allowing the fabrication of thin films by spin-coating, blending and doping of Eu-complexes in matrices, they have a tendency to show phase separation over time, leading to instability in the device's performance.¹¹ Fortunately, the problems can be avoided by the new approach of incorporating the Eu-complexes into the polymer matrix through covalent linkages. It is believed that through the covalent linkage with the polymeric host matrices the Eu-complex moieties can be dispersed more uniformly in the hosts, and more efficient energy transfer from the main chains to the Eucomplex moieties can be expected.12

Recently, Eu-containing polymers based on three β -diketone ligands and polymerizable neutral ligands, including carboxylic acids, 2,2'-bipyridine (bpy) and phenanthroline (phen) derivatives, have been focused on.¹³ Several results have shown that the maximum brightness is more than 10 cd m⁻², but the practical requirements for application still cannot be achieved. The reason for the low brightness for these PLEDs may be attributed to the neutral ligands being inferior in polymerization and often inducing an uncontrollable proportion of Eucomplexes in the copolymers. Therefore, the use of stable polymerizable Eu-chelated monomers is still imperative for efficient luminescent copolymers.

Terpyridine (tpy), a classic chelating tridentate ligand for transition metal and rare earth ions, has played an important role in the development of coordination chemistry and still continues to be of considerable interest as a versatile starting material for organic, inorganic and supramolecular chemistry.¹⁴ tpy is a rigid, planar, hydrophobic, electron-accepting heteroaromatic system, whose three nitrogen atoms are beautifully placed to act cooperatively in cation binding. These structural features determine its coordination ability toward metal ions. As is well-known, many studies have confirmed that tpy is an excellent neutral ligand for Eu-complexes; it can reduce the non-radiative decay of the excited states of the europium ion, improve the stability of the europium complexes, and increase the energy transfer efficiency from the ligands to the Eu³⁺ ions.¹⁵ Surprisingly, although photoluminescent property studies of many Eu-complexes based on tpy as a neutral ligand have been reported, we cannot find any one example of research into the electroluminescence of Eucomplexes based on tpy as a neutral ligand.

In this work, a novel polymerizable vinyl-tpy ligand 4'-(4-((4-vinylbenzyl)oxy)phenyl)-2,2':6',2''-terpyridine and the corresponding Eu-complex were designed and synthesized. Three copolymers, **P1**, **P2** and **P3** were prepared by using the Eu-complex and *N*-vinylcarbazole as the monomers with compositions of 1 : 100, 1 : 50 and 1 : 30. To enhance the ligand-mediated energy transfer, PVK with good hole transporting properties was chosen as the host segment. Dramatically high PL efficiencies of around 40% in the solid state were realized. A

remarkable solid emission amplification phenomenon was observed. Most importantly, the EL performances of eight pure red-emission PLEDs based on **P1**, **P2**, and **P3** as the emitting layer have been researched in detail. Bright electroluminescence with a maximum luminance of 68.2 cd m⁻² from the double-layer devices of **P1** was demonstrated. Although the EL performance is only third-best among those of the Eu-chelated polymers reported so far, to the best of our knowledge, this is the first example of electroluminescent devices (including small molecular Eu-complexes and Eu-polymer electroluminescent devices) of Eu-polymers based on tpy as a neutral ligand.

2 Experimental section

Materials and instruments

All reagents used were of analytical grade. DMF and acetonitrile were dried with CaH₂ for about 24 h and distilled at reduced pressure. FTIR spectra were recorded using a Tensor 27 (Bruker) Fourier Transform Infrared Spectrometer. Elemental analysis data were obtained from a Vario EL elemental analyzer. The molecular weight of the Eu-polymers was determined by Waters 1515-2414 GPC gel permeation chromatography, using THF as an eluent and polystyrene as the standard. Differential scanning calorimetry (DSC) was conducted on a Pyris Diamond TALAB system at a heating rate of 20 °C min⁻¹ under nitrogen. Thermogravimetric analysis was conducted with a NETZSCH TG 209F3 at a heating rate of 15 °C min⁻¹ under an N₂ atmosphere and over a temperature range from 35 to 650 °C. All the ESI-MS spectra were recorded in a LCQ DECA XP mass spectrometer. NMR spectra were recorded on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer with TMS as an internal standard. UV-vis absorption spectra were recorded on a Shimadzu spectrophotometer (UV 2550). Cyclic voltammetry (CV) measurements were made on a computer-controlled CHI600D electrochemical analyzer with a Pt working electrode, a Pt plate counter electrode, and an SCE reference electrode immersed in 0.1 M Bu₄NClO₄ in dry acetonitrile purged with dried argon. The scanning rate was 50 mV s^{-1} , and all electrochemical potentials were calibrated with the ferrocene/ferrocenium (Fc/Fc^{+}) standard. The photoluminescence (PL) measurements in the solid state and THF solution were conducted on a Hitachi F-4600 fluorescence spectrophotometer. Fluorescent lifetimes were obtained with an FLS920 steady state spectrometer with a pulsed xenon lamp.

4-(4-Vinylbenzyloxy)benzaldehyde. Solid KOH (2.25 g, 40 mmol) was added to a solution of 4-hydroxybenzaldehyde (4.89 g, 40 mmol) and 4-vinylbenzyl chloride (7.16 g, 40 mmol) in DMF (100 mL), and the mixture was stirred for 12 h at room temperature. Water (800 mL) was added to precipitate the product, which was isolated, washed with water (3×50 mL), and dried in a vacuum at 60 °C. Excess 4-vinylbenzyl chloride was removed by triturating the product in hexane (50 mL). The product was then washed with additional hexane (3×20 mL) and dried under a positive air flow. Yield: 8.11 g (85%). ¹H NMR (400 MHz CDCl₃): 5.14 (s, 2H); 5.27–5.29 (d, 1H, $J_{HH} = 11$); 5.75–5.80 (d, 1H, $J_{HH} = 18$); 6.69–6.76 (dd, 1H, $J_{HH} = 8$, $J_{HH} = 8$); 7.06–7.09 (d, 2H, $J_{HH} = 9$); 7.38–7.46 (dd, 4H, $J_{HH} = 8$, $J_{HH} = 8$);

7.83–7.85 (d, 2H, $J_{\rm HH}$ = 8); 9.89 (s, 1H). ESI-MS: m/z 242.4 (M + H)⁺. FTIR (KBr pellet, cm⁻¹): 2935, 1706 (C=O stretching), 1601, 1512, 1380, 1261, 1160, 1008, 832.

4'-(4-((4-Vinylbenzyl)oxy)phenyl)-2,2':6',2"-terpyridine (vinyltpy). 2-Acetylpyridine (2.42 g, 20 mmol) was added into a solution of 4-(4-vinylbenzyloxy)benzaldehyde (2.38 g, 10 mmol) in EtOH (100 mL). KOH pellets (1.55 g, 85%, 20 mmol) and aqueous NH₃ (30 mL, 29.3%, 25 mmol) were then added to the solution. The solution was stirred at room temperature for 12 h. The milk-white solid was collected by filtration and washed with EtOH (3 \times 20 mL). Yield: 2.73 g (62%). ¹H NMR (400 MHz CDCl₃): 8.65-8.71 (m, 6H, tpy), 7.83-7.88 (t, 4H, ArH), 7.40-7.45 (m, 4H, ArH), 7.26-7.33 (t, 2H, tpy), 7.07-7.09 (d, 2H, ArH), 6.70-6.77 (m, 1H, CH=CH₂), 5.75-5.80 (d, 1H, CH=CH₂), 5.25-5.28 (d, 1H, CH=CH₂), 5.08 (s, 2H, -CH₂-). ¹³C NMR (100 MHz CDCl₃): 159.5, 156.2, 155.7, 149.5, 148.9, 137.1, 136.8, 136.3, 130.9, 128.4, 127.7, 126.4, 123.7, 121.3, 118.2, 115.1, 114.1, 69.7. ESI-MS: m/z 442.3 (M + H)⁺. FTIR (KBr pellet, cm⁻¹): 1603, 1584, 1566, 1513, 1463, 1386, 1252, 1183, 1038, 992, 830, 793, 734.

Preparation of the europium monomer Eu(TTA)₃vinyl-tpy (EuVTPY). The complex was prepared according to the wellestablished method.16 Vinyl-tpy (0.44 g, 1 mmol) was dissolved in THF (50 mL), to which Eu(TTA)₃·2H₂O (0.85 g, 1 mmol) was added. The whole mixture was refluxed for 3 h and cooled to room temperature. The resulting precipitate was collected and washed twice with water to give the target complex (0.93 g, 74%)as a light-yellow powder. (Found: C, 50.08; H, 2.94; N, 3.19. EuC₅₄H₃₅F₉N₃O₇S₃ [EuVTPY] requires C, 51.60; H, 2.81; N, 3.35%). ¹H NMR (400 MHz CDCl₃): 14.34 (s, 2H, tpy), 12.87 (s, 2H, tpy), 11.20 (s, 2H, tpy), 10.76 (s, 2H, tpy), 8.19 (s, 2H, ArH), 7.24-7.68 (m, 4H, ArH), 6.95 (s, 2H, ArH), 6.82-6.85 (m, 3H, Th-H), 6.72-6.79 (m, 1H, CH=CH₂), 6.48 (m, 3H, Th-H), 6.28 (s, 2H, Th-H), 5.61-5.68 (m, 4H, CH=CH₂), 5.23-5.27 (m, CH= CH₂), 5.14 (s, 2H, CH₂). ESI-MS *m/z*: [Eu(TTA)₂vinyl-tpy]⁺ calculated for EuC₄₆H₃₁F₆N₃O₅S₂, 1036.08; found, 1036.0. FTIR (KBr pellet, cm⁻¹): 1617 (C=O stretching in TTA), 1538 (C=C stretching in TTA), 1417, 1312, 1188, 1139, 1058, 780.

Preparation of the Eu-chelated copolymers (Eu-polymer P1, P2 and P3). A mixture of N-vinyl carbazole (0.51 g, 2.6 mmol), EuVTPY (33 mg, 0.027 mmol for P1, 68 mg, 0.054 mmol for P2, and 113 mg, 0.090 mmol for P3), and AIBN (2,2'-azobisisobutyronitrile) initiator (6 mg, about 1 wt% of the total monomers) was dissolved in dry DMF (3 mL) in a glass polymerization tube. The homogeneous solution was purged with argon for 5 min and sealed under a reduced argon atmosphere. The mixture was heated to 65 °C with continuous stirring for 24 h. The reaction mixture remained clear throughout the copolymerization process. The viscous mixture was diluted with DMF (3 mL) and precipitated into methanol (50 mL) under vigorous stirring. The reprecipitation procedure was repeated three times. The resulting solid material was collected by filtration. The copolymer was further purified by Soxhlet extraction with boiling acetone for 48 h and finally dried in a vacuum oven at 60 °C for 24 h. The feed ratios in the polymerization experiments are shown in Table S1.†

P1: with yield of 0.45 g (83%) as milk-white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.68, 7.39, 6.89, 6.44, 4.88, 3.41, 3.21, 2.56, 2.19, 1.66–1.73, 0.87–1.53 ppm. ¹³C NMR (100 MHz, CDCl₃):

δ 162.51 (carbon of Ar), 156.43 (carbon of tpy), 155.89 (carbon of tpy), 149.12 (carbon of tpy), 139.96 (carbon of carbazole), 137.25 (carbon of carbazole), 125.06 (carbon of carbazole), 123.66 (carbon of carbazole), 121.86 (carbon of carbazole), 120.10 (carbon of carbazole), 110.18 (carbon of carbazole), 107.96 (carbon of carbazole), 102.25, 69.81 (carbon of ethyl), 65.05 (carbon of TTA). FTIR (KBr pellet, cm⁻¹): 1601, 1536 (C=C stretching in TTA), 1492, 1455, 1329, 1221, 1158, 1124, 747, 718. Elemental analysis calcd (%): C 83.94, H 6.43, N 6.94. Found: C 84.12, H 6.27, N 7.04. Molecular weight: $M_n = 10$ 053, $M_w = 18$ 438, PDI = 1.83. Content of Eu³⁺ = 0.73 wt%. Polymer composition: n : m = 1 : 100, determined according to the results of elemental analysis and Eu³⁺ titration.

P2: with yield of 0.38 g (65%) as milk-white powder. ¹H NMR (400 MHz, CDCl₃): δ 8.05, 7.68, 7.43, 6.97, 6.89, 6.50, 6.37, 4.77, 3.50, 3.16, 2.48, 1.40–1.92, 0.94–1.24 ppm. ¹³C NMR (100 MHz, CDCl3): δ 162.50, 156.43, 155.90, 149.11, 139.93, 137.22, 125.06, 123.56, 121.87, 120.13, 118.95, 110.16, 107.96, 102.25, 69.83, 65.04 (carbon of TTA). FTIR (KBr pellet, cm⁻¹): 1600, 1536 (C=C stretching in TTA), 1484, 1451, 1336, 1227, 1159, 1124, 743, 719. Elemental analysis calcd (%): C 82.09, H 6.23, N 6.73. Found: C 82.15, H 6.06, N 6.85. Molecular weight: $M_n = 8228$, $M_w = 15367$, PDI = 1.87. Content of Eu³⁺ = 1.38 wt%. Polymer composition: n : m = 1 : 50, determined according to the results of elemental analysis and Eu³⁺ titration.

P3: with yield of 0.32 g (51%) as milk-white powder. ¹H NMR (400 MHz, CDCl₃): δ 8.74, 8.09, 7.99, 7.51, 7.68, 6.98, 6.44, 6.50, 5.14, 4.89, 3.48, 3.16, 2.72, 0.86–1.75 ppm. ¹³C NMR (100 MHz, CDCl₃): δ 162.48, 156.43, 155.81, 149.15, 139.98, 137.21, 125.06, 123.69, 121.86, 120.05, 118.95, 110.15, 107.96, 102.18, 69.81, 65.01. FTIR (KBr pellet, cm⁻¹): 1601, 1536 (C=C stretching in TTA), 1484, 1333, 1222, 1160, 747, 726. Elemental analysis calcd (%): C 79.92, H 5.99, N 6.49. Found: C 80.01, H 5.87, N 6.55. Molecular weight: $M_{\rm n} = 6226, M_{\rm w} = 10$ 396, PDI = 1.67. Content of Eu³⁺ = 3.69 wt%. Polymer composition: n : m = 1 : 30, determined according to the results of elemental analysis and Eu³⁺ titration.

Calculation of quantum efficiency (η) in solid state. The intrinsic fluorescent quantum efficiency (η) of the ⁵D₀ emission level in EuVTPY, **P1**, **P2**, and **P3** at room temperature was obtained based on the luminescence data (emission spectra and emission decay curves of these Eu-complexes). Eqn (1) is a means to determine the η values from experimental spectroscopic data:²⁵

$$\eta = \frac{A_{\rm rad}}{A_{\rm rad} + A_{\rm nrad}} \tag{1}$$

where, $A_{\rm rad}$ and $A_{\rm nrad}$ are radiative and nonradiative transition rates, respectively. The denominator in eqn (1) is calculated from the lifetime of the emitting level ($1/\tau = A_{\rm rad} + A_{\rm nrad}$). In the case of europium fluorescence the value of $A_{\rm rad}$ can be estimated by spectral analysis with the help of eqn (2):

$$A_{\rm rad} = \frac{A_{0-1}h\omega_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{h\omega_{0-J}}$$
(2)

where, *J* represents the final ${}^{7}F_{0-6}$ levels, *S* is the integrated intensity of the particular emission lines and $h\omega$ stands for the

corresponding transition energies. A_{0-1} is the Einstein coefficient of spontaneous emission between the ⁵D₀ and the ⁷F₁ Stark levels. The branching ratios for the ⁵D₀ \rightarrow ⁷F_{5,6} transitions must be neglected as they are too weak to be observed experimentally. Therefore, their influence can be ignored in the depopulation of the ⁵D₀ excited state. The ⁵D₀ \rightarrow ⁷F₁ transition is independent of the local ligand field seen by the europium ions and, thus, may be used as a reference for the whole spectrum, *in vacuo* $A_{0-1} = 14.65 \text{ s}^{-1}$.²⁶ An average refractive index equal to 1.5 was considered, leading to $A_{0-1} \approx 50 \text{ s}^{-1}$.

Calculation of quantum yield (Φ) in THF solution. Solution fluorescent yields of EuVTPY, P1, P2, and P3 were determined using quinine sulfate (dissolved in 0.5 M H₂SO₄ with a concentration of 10⁻⁶ M, assuming $\Phi_{\rm PL}$ of 0.55) as a standard.²⁷ The quantum yield was calculated according the following equation:

$$\Phi = \Phi_{\rm r} \frac{A_{\rm r}}{A} \frac{S}{S_{\rm r}} \frac{n^2}{n_{\rm r}^2} \tag{3}$$

where Φ is the fluorescence quantum yield, *S* represents the area of the corrected emission fluorescence spectrum, *A* is the absorbance of the solution at the excitation wavelength, and *n* is the refractive index of the solvent used. The subscript r denotes the reference substance whose fluorescence quantum yield is already known.

Fabrication and testing of PLEDs. Single-layer and doublelayer PLEDs were fabricated by spin coating with three configurations of ITO/PEDOT (40 nm)/Eu-polymer (80 nm)/Ba (4 nm)/ Al (120 nm), ITO/PEDOT (40 nm)/PVK (40 nm)/Eu-polymer (80 nm)/Ba (4 nm)/Al (120 nm) and ITO/PEDOT (40 nm)/Eu-polymer:OXD-7 (30%, 40%, 80 nm)/Ba (4 nm)/Al (120 nm), where PEDOT is poly(3,4-ethylenedioxythiophene) as the hole injection material, OXD-7 is 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxidiazolyl]phenylene as the electron-transporting material, and ITO and Ba/Al were used as the anode and cathode, respectively. PLED was fabricated on patterned indium tin oxide (ITO) with a sheet resistance of 15–20 Ω per square. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol. Oxygen plasma treatment was applied for 4 min as the final step just before film coating. Onto the ITO glass was spin-coated a layer of PEDOT film with a thickness of 40 nm from its aqueous dispersion. The PEDOT film was dried at 80 °C for 3 h in a vacuum oven. The solution of the polymer was prepared under nitrogen atmosphere and spin-coated onto the PEDOT layer. The typical thickness of the emitting layer was 80 nm. Then a thin layer of barium as an electron injection cathode and the subsequent 140 nm thick aluminum protection layers were thermally deposited by vacuum evaporation through a mask at a base pressure below 2 \times 10 $^{-4}$ Pa. The cathode area defines the active area of the device. The typical active area of the devices in this study is 0.15 cm². The EL layer spin coating process and the device performance tests were carried out within a glovebox under a nitrogen atmosphere. Currentvoltage (I-V) characteristics were recorded with a Keithley 236 source meter. EL spectra were obtained by an Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (Photo Research). The external quantum

efficiencies were determined by a Si photodiode with calibration in an integrating sphere (IS080, Labsphere).

3 Results and discussion

3.1 Geometry optimization, and simulation of UV and IR spectra for EuTPY

In the field of coordination compounds, the semiempirical Sparkle/PM6 model has proven to be effective in lanthanide chemistry because it allows the prediction of the coordination geometry for both small lanthanide complexes and more sophisticated structures in a relatively short time and with a low computational demand.17 Recent results have shown good prediction for the ground state geometry, when compared to single crystal data.18 Here the ground state geometry shown in Fig. S1[†] was calculated using Sparkle/PM6 implemented in the Mopac2012 package. The Sparkle model replaces the lanthanide ion by a core with +3e charge, so that only the electrostatic interaction between the ion and the ligand is considered. The Eu³⁺ ion in this compound is nine-coordinate and the coordination polyhedron can be approximately described as a tricapped trigonal prism, and the europium complex belongs to the C_1 point-group. The structural parameters of the coordination polyhedron, shown in Table S2,† are given by the distance between the europium ion and ligand (R), the angle between the z axis and the ligand atom (θ) and the angle of the projection of vector **r** in the xy plane and the x axis (φ). The average distance for Eu-O (TTA) of 2.403 and Eu-N (tpy) of 2.551 Å are close to the distances estimated using X-ray diffraction data for the corresponding single crystal Eu-complex based on TTA and terpyridyl derivatives.19

As is well known, knowledge of the location of orbitals in luminescent lanthanide research is important. Therefore we calculated the molecular orbitals (MOs) of EuVTPY using Gabedit software using the optimized data by Mopac2012. Fig. 1(a) and (b) show the HOMO and LUMO of EuVTPY; the calculated results indicate that the HOMO is mostly localized on the vinylbenzene moiety, and the LUMO is mostly localized on the tpy group. Molecular magnets are a very active research area. Recently, there has been interest in the development of molecular magnets with paramagnetic lanthanide ions.20 Fig. 1(c) shows the spin density distribution along the EuVTPY molecule, the blue balloons are considered to be regions where the spin density is positive and the red balloons are the regions where the spin density is negative. It is seen that the spin density of the Eu-complex is mainly located at the vinylbenzene moieties, and is mostly negative; meanwhile, little positive spin density in the vicinity of the para-C-C of the benzene group can be found. The electron density distribution of EuVTPY is displayed in Fig. 1(d);the distribution of the electron density in this complex is very interesting, it is mostly located on the vinylbenzene and TTA moieties, however, electron density in the tpy moiety almost cannot be observed. Obtaining the electron density distribution may help understand the energy transfer progress, and will be studied in detail in future work.

The experimental and simulated FTIR spectra of the monomer EuVTPY are shown in Fig. S2.[†] The calculation was made



Fig. 1 (a) HOMO and (b) LUMO of the monomer EuVTPY. The red and blue lobes denote the positive and negative phases of the coefficients of the molecular orbitals. The size of each lobe is proportional to the MO coefficient. (c) Calculated spin density distribution at the EuVTPY surface (the blue balloons indicate regions where the spin density is positive and the red balloons the regions where the spin density is negative). (d) Calculated electronic density distribution at the EuVTPY surface. (Light green, black, blue, pink, blue-green, yellow, and red balls correspond to hydrogen, carbon, nitrogen, oxygen, fluorine, sulfur, and europium atoms, respectively.)

for a free molecule in vacuum, while the experiment was performed for the solid state; furthermore, the anharmonicity in the real system was neglected for the vibration calculations. Therefore, they are disagreements between the calculated and experimental vibrational wavenumbers. Nevertheless, the characteristic stretching peaks of EuVTPY can be realized, these absorbance peaks located at 1725, 1640 and 1453 cm⁻¹ are attributed to the C=O and C=C stretching vibrations of the coordinated TTA ligand and C=N of the coordinated vinyl-tpy ligand in the Eu-complex, respectively. A comparison of the calculated and experimental UV spectra for the monomer EuVTPY is presented in Fig. S3.[†] As can be seen, the agreement between the simulated and experimental spectra is very good. Whether in the calculated or in the experimental spectrum, two main absorption bands of the monomer EuVTPY are easily observed, which are attributed to the singlet-singlet $\pi \to \pi$ enol absorption of TTA and tpy moieties in the monomer Eucomplex. It is noteworthy that the last absorption band (located at near 344 nm) in the simulation is very similar to that in the experiment. However, an obvious red shift of the first absorption band in the calculated spectrum can be observed, which might be attributed to the solvent effects neglected in the calculation or any errors inherent in the method itself.

3.2 Design, synthesis, and characterization

With the aim of developing the first PLEDs of Eu-polymers based on tpy as a neutral ligand, a novel tridentate ligand vinyltpy and a corresponding polymerizable monomer EuVTPY have been designed and synthesized. To increase the energy transfer efficiency from the ligand to the emission center of the Eu³⁺ ions, blue-emitting PVK (which possesses good hole transporting properties) was chosen as the host segment in these Eupolymers. Most importantly, due to the neutral ligand vinyl-tpy has a strong coordination ability, structure adjustment ability, protuberant coordinate sites and inertia towards modification, so we predict that the monomer EuVTPY and the corresponding Eu-polymers P1, P2 and P3 will have excellent PL and EL properties. The synthesis procedures of EuVTPY and P1, P2 and P3 are outlined in Scheme 1. In the first step, 4-(4-vinylbenzyloxy)benzaldehyde is obtained from 1-(chloromethyl)-4vinylbenzene and 4-hydroxybenzaldehyde reacting in DMF in the presence of KOH at room temperature in a high yield (85%). 4'-(4-((4-Vinylbenzyl)oxy)phenyl)-2,2':6',2''-terpyridine formed by the condensation of 2-acetylpyridine and 4-(4-vinylbenzyloxy)-benzaldehyde, according to a slightly modified tpy derivate preparation method.²¹ The chromophore monomer EuVTPY was synthesized according to the well-established procedure with a high yield of 74%. The Eu-polymers P1, P2 and P3 were prepared by the classic free radical copolymerization of EuVTPY and N-vinvlcarbazole (NVK), using AIBN as the initiator, in dry DMF. All of the compounds were characterized by NMR, ESI-MS, FTIR, and elemental analysis.

Compared with the ligand vinyl-tpy, in the FTIR spectrum of polymerizable EuVTPY, three new absorbance peaks were observed at 1613, 1538 and 1413 cm^{-1} (Fig. 2). They are attributed to the C=O and C=C stretching vibrations of the coordinated TTA ligand and the C=N stretching vibration of the coordinated vinyl-tpy ligand in the Eu-complex, respectively. These results indicate that the neutral ligand vinyl-tpy and the ionic ligands TTA had successfully coordinated with the Eu³⁺ ion emission centers. The FTIR spectra of the Eu-polymers are shown in Fig. 2, and are very similar to the FTIR spectrum of pure PVK. Two sharp and strong absorption peaks at 750 and 722 cm^{-1} are attributed to the characteristic absorptions of the carbazole moieties. Because of the formation of polymer and the low content of EuVTPY in the polymers, the strong and widely-dispersed absorption peaks of the PVK segments almost cover all of the characteristic absorption peaks of EuVTPY, such as the TTA absorption band at 1613 cm⁻¹. Fortunately, covalent attachment of the Eu-complex unit to the polymer backbone is strongly supported by the C=C stretching vibrations of the coordinated TTA ligand around 1536 cm^{-1} , which is a strong absorption peak in the spectrum of EuVTPY and a much weaker peak in those of the Eu-polymers.

GPC analysis (using poly-styrene as the standard for calibration) showed that the number-average molecular weight (M_n) and polydispersity indexes (PDI) of the Eu-polymers are 10 053, 1.83 for P1, 8228, 1.87 for P2, and 6226, 1.67 for P3. The appropriate molecular weight and relative narrow PDI are beneficial to form uniform thin films and enhance the mechanical capacities of the films. According to the results of the elemental analysis and titration experiments, the compositions of the copolymers (n : m molar ratio) were about 1 : 100, 1:50 and 1:30. The feed ratios of Eu-polymer are very close to its actual composition, which means that the reactivity of EuVTPY to NVK is similar with the reactivity between NVKs. However, it is noticed that the molecular weight and yield of the copolymers remarkably decrease along with an increase of the EuVTPY : NVK feed ratio. In addition, the differences between the copolymer compositions and the feed ratios increase from P1 to P3. The main reason might be that along with the increase of the molar quantity of EuVTPY, the possibility of collision

Paper



Scheme 1 Synthetic procedures of the monomer EuVTPY and Eu-polymers P1, P2 and P3



Fig. 2 The FTIR spectra of vinyl-tpy, monomer EuVTPY and Eu-polymers.

between EuVTPY units also increases. Although the tridentate tpy ligand has a suitable structure, the polymerization between bulky EuVTPY molecules is much more difficult than that between EuVTPY and NVK. Thus, these collisions might induce chain termination or chain transfer, which reduce the molecular weight of **P2** and **P3**. The resulting copolymers are readily soluble in common organic solvents, such as THF, dichloromethane, chloroform and toluene, and can be easily cast into transparent and uniform thin films.

The ¹H NMR spectrum of the Eu-polymer P2 obtained at 400 MHz in chloroform solution is shown in Fig. 3. The spectrum consists of several broad peaks with chemical shifts in the ranges of 4.5-8.0 and 0.50-4.0 ppm, which are associated with the aromatic and alkyl protons, respectively. It has been reported that the two aromatic rings of the carbazole group are magnetically non-equivalent, despite the fact that the carbazole moiety belongs to the C_{2v} symmetry group.^{22,32} This phenomenon is due to the fact that, in the polymer chain, the neighboring carbazole units may be partially or totally overlapped in different stereochemical sequences (meso or racemic conformations, as shown in structure (a) of Fig. 3); similar phenomena have been observed in poly(c-glutamic acid) ester systems.³³ The non-equivalence of the two carbazole rings is reflected in the ¹H NMR spectrum. For example, the more severely shielded proton H1 appears in the high field region (4.87 ppm), while the proton H8 of the less severely shielded ring appears at 6.35 ppm. The ring current effect is the main contribution to this difference in chemical shifts. The other peaks in the specified low field region are reasonably assigned to the aromatic protons. The



Fig. 3 ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra of P2 in CDCl₃. (a) The meso (m) and racemic (r) conformations of the neighboring carbazole (Cz) units; (b) the head-to-tail (h–t), tail-to-tail (t–t) and head-to-head (h–h) sequences in the polymer chain.

resonances of methenyl protons (H9, H11) and methylene protons (H10, H12) in the polymer backbone appear with multipeaks in the regions of 2.4–3.5 ppm and 1.1–1.7 ppm, respectively. This observation is attributed to the existence of different stereo-chemical sequences in the polymer chain (structures (a) and (b)). Due to a low content of EuVTPY in the Eu-polymers, the chemical shifts of the protons in the TTA and tpy groups are weak and buried by those of the carbazole group.

The chemical shifts in the 13 C NMR spectrum of Eu-polymer **P2** are expanded in several regions (Fig. 3). The non-equivalence of the two carbazole rings is also reflected in the carbon chemical shifts. Chemical shifts for all the different carbon species in the carbazole units are clearly shown in the 12 groups of broad peaks.^{23,32} The resonance of carbon C9, which is bonded to a nitrogen atom, appears clearly as three peaks located at 48.2, 49.1 and 50.1 ppm. These three chemical shifts correspond to the *isotactic* (mm), *syndiotactic* (rr) and

heterotactic (mr) sequences existing in the polymer chain. The other aliphatic carbon atoms (C10-C12) resonate at a higher field (33-40 ppm), compared to that of carbon C9. Again, the resonance signals of the carbon atoms in the ligands TTA and vinyl-tpy, which are located in the resonance region of the carbazole carbons, are difficult to recognize. However, the ethyl carbon (C17) and phenyl carbon (C18) of the vinyl-tpy are bonded to an electron-withdrawing atom (O) and the resonance is, therefore, shifted to lower field, compared to the normal ethyl carbon and phenyl carbon. Owing to the effects of the oxygen atoms bonded to the two neighboring carbon atoms, the aliphatic carbon (C22) of the TTA group is also detected at a lower field (at about 63 ppm), compared to the other aliphatic carbon atoms in the backbone. In addition, due to the effect of electron-withdrawing atoms (N), the carbons C19, C20 and C21 of the tpy groups are observed at low field, and are located at about 156.4, 155.9 and 149.2 ppm, respectively. Based on the

above, the NMR results further confirm the successful formation of the designed Eu-polymers.

3.3 Thermal properties

The thermal stability of the Eu-complexes is very important because decomposition leads to decreased EL performance. The differential scanning calorimetry (DSC) analysis of the Eupolymer was measured to investigate their phase stability (Fig. 4). The glass transition temperature (T_g) of **P1** is 171.7 °C, which is lower than that of the PVK homopolymer ($T_{\rm g} = 200$ °C). It is noted that the $T_{\rm g}$ values of **P2** and **P3** are reduced to 163.5 °C and 143.1 °C, respectively, which means that the rigidity of the Eu-polymers was reduced with increasing Eu-chelated content. The T_{g} values of **P2** and **P3** are lower than that of **P1**, and this can be ascribed to the increase of the content of Eu-chelated moieties accompanied with the steric effect of the related macromolecular monomer EuVTPY and the disruption of the ordered structures of the entire polymers. Nevertheless, the phase stability of P1, P2 and P3 is still favorable among the soluble light-emitting polymers. The thermal stability of Eupolymers was investigated by thermogravimetric analysis (TGA) (Fig. 5). The temperatures of the thermal decomposition (T_d , 5% weight loss temperature) of P1, P2 and P3 are 294.8, 276.9 and 261.1 °C, respectively, which are lower than that of PVK (439 °C). Obviously, since the coordinate bond is much weaker, the initial decomposition process mainly involves the rupture of the O-Eu bond in EuVTPY and decomposition of Eu(TTA)₃. Nevertheless, P1, P2 and P3 still have good thermal stability with 5% weight loss occurring at greater than 260 °C.

3.4 Optical properties

The UV-vis absorption spectra for vinyl-tpy, EuVTPY, P1, P2 and P3 in THF solution $(1 \times 10^{-5} \text{ mol L}^{-1})$ are shown in Fig. S4[†]. Two main absorption bands of the monomer EuVTPY are easily observed, at 286 nm and 344 nm, which are attributed to the singlet–singlet $\pi \rightarrow \pi$ enol absorption of TTA and tpy moieties



in the monomer Eu-complex. Due to the formation of larger conjugated chelate rings in EuVTPY, those main absorption bands shift to longer wavelengths compared with corresponding ligands. Because the content of Eu³⁺ chelated segments in the polymers is rather small, in the UV-vis absorption spectra of **P1**, **P2** and **P3** in dilute THF solution, all of the absorption bands from the monomer EuVTPY are completely buried by the strong bands at 250, 260, 294, 330, and 344 nm corresponding to the transitions of the carbazole groups.

The excitation spectra of EuVTPY, **P1**, **P2** and **P3** in a solid and in THF solution were obtained by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of the europium ion, which is shown in Fig. 6 and 7. For solution excitation spectra, one broad excitation band at 288–404 nm can be easily observed for EuVTPY, **P1**, **P2** and **P3**. In the solid state excitation spectra, it can be seen clearly that the intense broad band between 200 nm and 423 nm dominates large portions of the excitation spectra of all the Eu-complexes, which is attributed to the $\pi \rightarrow \pi^{*}$ transitions of TTA, tpy, and



Fig. 4 DSC curves of P1, P2 and P3.



Fig. 6 The PL spectra of EuVTPY and **P1**, **P2**, and **P3** in the solid state. Left: excitation spectra ($\lambda_{em} = 615$ nm), right: emission spectra ($\lambda_{ex} = 360$ nm) (\bigstar : false peak).

the carbazole moieties from the comparison of the UV-vis spectra in Fig. S4.† In particular, in the excitation spectrum of the monomer EuVTPY in the solid state, other than the intense broad bands, a weak excitation peak was also observed at 465 nm, which results from the ${}^5D_0 \rightarrow {}^7F_2$ transition of the europium ion. In comparison with the excitation broad bands of the ligands, the direct excitation peaks of the Eu $^{3+}$ ions were much weaker. This result suggests that fluorescence sensitization by excitation of the ligands was much more efficient than direct excitation of the Eu $^{3+}$ ion absorption levels.

The PL spectra of the monomer EuVTPY, P1, P2 and P3 in THF solution $(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ are shown in Fig. 7. As with most Eu-chelated PVK copolymers, the PL spectra of P1, P2 and P3 in THF solution consist of two groups of emission peaks. The first group from about 350 to 500 nm contains the emission bands originating from $\pi^* \rightarrow \pi$ transitions of the carbazole moieties. The second group comprises the characteristic emissions of Eu-chelated compounds at 580, 594, 615, 653 and 697 nm, which originate from the Eu^{3+} ion corresponding to ${}^{5}D_{0}$ \rightarrow ⁷F_i (*j* = 0-4) transitions. For the Eu-polymer **P1**, due to the content of EuVTPY units being rather low, the emission of carbazole is much stronger than that in P2 and P3, and the color as observed by the naked eye in THF solution appears pink under UV 365 nm excitation (Fig. 8), and the CIE chromaticity coordinates from the emission spectra are (0.31, 0.12). For P2 and P3, with the content of EuVTPY units increasing, the emission intensity of carbazole gradually decreases, and the color changes from pink (P1) to pure red (P3), and the CIE coordinates are (0.58, 0.28) and (0.60, 0.29) for P2 and P3, respectively. Fig. 6 shows the PL spectra of the monomer EuVTPY, P1, P2 and P3 in the solid state. In contrast to the PL spectra of the Eu-polymer P1, P2 and P3 in solution, the PL spectra of the Eu-polymer is dominated by red emission from the EuVTPY moieties. For the Eu-polymers P1, P2 and P3 in the solid state, the blue emission attributed to the PVK sequences is too weak to be recognized. The molecular aggregation in the



Fig. 7 The PL spectra of EuVTPY and **P1**, **P2**, and **P3** in THF solution (1×10^{-5} mol L⁻¹). Left: excitation spectra ($\lambda_{em} = 615$ nm), right: emission spectra ($\lambda_{ex} = 359$ nm).

View Article Online Journal of Materials Chemistry C



Fig. 8 Left: CIE coordinate diagram of EuVTPY, P1, P2, and P3 in the solid state and in THF solution. Right: luminescent image of Eu-complexes excited at 365 nm in the solid state and in THF solution.

solid enhances the intermolecular interactions, which facilitates the inter- and intrachain Förster energy transfer. Moreover, the shorter intermolecular distance and the more effective inter- and intrachain winding and wrapping of Eu-chelated moieties increase the possibility of electron overlap between the PVK sequences and the EuVTPY segments, which consequently improves the Dexter-type energy transfer. Thus, in the solid state the strong intermolecular interactions remarkably facilitate the energy transfer from the blue-emitting PVK sequences to the red-emitting EuVTPY moieties. Because the copolymer is designed to have integration between the host and guest, the high efficiency energy transfer between the different moieties is the basis of the high performance of the PL and EL. Although the Eu-complex content is low (ca. 0.73% for P1, 1.38 for P2, and 3.69 for P3) in these Eu-polymers, the energy transfer is also highly efficient. Therefore, finding the balance point between efficient host-guest energy transfer and limited concentration quenching is most likely. In addition, the monomer EuVTPY and the Eu-polymers (P1, P2 and P3) exhibit characteristic red emission of europium ions under UV 365 nm (Fig. 8) excitation, and it is suggested that these complexes can be potential red fluorescent materials. The CIE chromaticity coordinates of EuVTPY, P1, P2, and P3 from the emission spectra are (0.67, 0.33), (0.61, 0.30), (0.66, 0.32) and (0.66, 0.33) in the solid state, respectively, which indicates pure red emission. The results are important because they indicate an advantage for rare-earth complexes for preparing PLEDs.

Whether in the solid state or in THF solution, the intensity ratios (I_2/I_1) of these Eu-complexes were very high. In the solid state, the intensity ratios (I_2/I_1) of EuVTPY, **P1**, **P2** and **P3** were 11.35, 12.10, 12.54, and 14.21, respectively, and in THF solution they were 16.49, 12.47, 13.86, and 14.08, respectively. This ratio was only possible when the Eu³⁺ ion did not occupy a site with inversion symmetry. It was clear that strong coordination interactions took place between the ligands and Eu³⁺ ion. Furthermore, the emission spectra of the complexes showed only one line for the ${}^5D_0 \rightarrow {}^7F_0$ transition, indicating the

presence of a single chemical environment around the europium ions.²⁴

To better understand the fluorescent properties of EuVTPY, **P1**, **P2** and **P3** in the solid state and in THF solution, the room temperature (RT) fluorescence decay curves of the 5D_0 excited state were measured by monitoring the most intense emission lines (${}^5D_0 \rightarrow {}^7F_2$) of the europium ion center at 616 nm, and under excitation by a 360 nm Xenon lamp. As shown in Fig. S5,† whether in a solid or in THF solution, the decay curves of the complexes exhibited monoexponential behavior, indicative of the presence of a single chemical environment around the Eu³⁺ ion in these Eu-complexes, which was in agreement with the results of only one ${}^5D_0 \rightarrow {}^7F_0$ line in the emission spectra and the calculated results of Sparkle/PM6. The fluorescent lifetime values (τ) of EuVTPY, **P1**, **P2**, and **P3** are 0.63, 0.60, 0.63 and 0.74 ms in the solid, and 0.48, 0.49, 0.50 and 0.56 ms in THF solution, respectively.

The fluorescent quantum efficiency (η) in the solid and quantum yield (Φ) in THF solution of EuVTPY, **P1**, **P2**, and **P3** at room temperature were calculated and are shown in Table 1.

In the solid state, the monomer EuVTPY, P1, P2 and P3 exhibited high fluorescent quantum efficiency; the values are 37.92, 38.21, 42.49, and 51.07%, respectively. These results show that, although the content of Eu³⁺ units in copolymer P1, P2 and P3 is very low (0.73, 1.38, and 3.69%, respectively), the quantum efficiency is higher than that of monomer EuVTPY. This is attributed to the fact that the carbazole is an efficient hole transport unit. After inducing the carbazole units into the Eu-polymers, the energy transfer can be more efficient than that in EuVTPY. In particular, the η of P3 is higher by about 13% that of EuVTPY, and this further confirms that the energy transfer from PVK sequences to the Eu³⁺ ion emission centers was very efficient in Eu-polymers P1, P2 and P3. In THF solution, the quantum yield (Φ) of monomer EuVTPY is relatively high (8.22%), however, the Φ of **P1** is only 1.31, which is far lower than that of EuVTPY. It can be interpreted that the interactions between the THF molecules and Eu-polymer P1 increase the distance between the PVK moieties and the Eu³⁺ ion emission center, disrupting the inter- and intrachain Förster energy transfer. In addition, the THF molecule vibration can reduce the quantum yield in THF solution. With the content of EuVTPY moieties in the Eu-polymer increasing, the Φ gradually increases; when the content of EuVTPY moieties is up to 3.69%, the ϕ of P3 is higher than that of the monomer EuVTPY.

To investigate the possible structural changes around the ${\rm Eu}^{\scriptscriptstyle 3+}$ ion emission centers among these Eu-complexes, the

Judd–Ofelt intensity parameters Ω_2 and Ω_4 can be calculated from the emission spectra as in ref. 28. In particular, Ω_2 is more sensitive to the symmetry and sequence of ligand fields. To obtain faster europium radiation rates, antisymmetrical europium complexes with large Ω_2 parameters need to be designed. The spontaneous emission probability $A_{0-\lambda}$ ($\lambda = 2, 4$) of the transitions are related to its dipole strength according to the equation:

$$A_{0-\lambda} = (64\pi^4 \nu^3)/[3h(2J+1)]\langle |n(n^2+2)/9|S_{\rm (ED)} + S_{\rm (MD)}\rangle \qquad (4)$$

Here, ν is the average transition energy in cm⁻¹, h is the Planck constant, and 2J + 1 is the degeneracy of the initial state. $S_{(ED)}$ and $S_{(MD)}$ are the electric dipole strength and magnetic dipole strengths, respectively. Among all these transitions, the ${}^{5}D_{0} \rightarrow {}^{7}F_{0,3,5}$ transitions are forbidden both in magnetic and electric dipole schemes ($S_{(ED)}$ and $S_{(MD)}$ are zero). In addition, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is the isolated magnetic dipole transition and has no electric dipole contribution, which is practically independent of the lanthanide ion chemical environment and can be used as a reference. The Judd–Ofelt parameters Ω_{2} and Ω_{4} can be calculated according to the equation:

$$\mathcal{Q}_{\lambda} = \frac{3hc^{3}A_{0-\lambda}}{4e^{2}w^{3}\chi\left\langle {}^{5}\mathbf{D}_{0} \|\mathbf{U}^{(\lambda)}\|^{7}\mathbf{F}_{J}\right\rangle^{2}}$$
(5)

where e is the electronic charge and w is the angular frequency of the transition. $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorenz local field correction. The square reduced matrix elements are $\langle {}^{5}D_{0} \| U^{(2)} \| F_{2} \rangle^{2} = 0.0032$ and $\langle {}^{5}D_{0} \| U^{(4)} \| F_{4} \rangle^{2} = 0.0023$, and an average index of refraction equal to 1.5 was used. The Ω_2 and Ω_4 intensity parameters for all Eu-complexes are shown in Table 1. A point to be noted in the results is the relatively high Ω_2 parameter for all Eu-complexes. In particular, it is evident that the Eu-polymers P1, P2 and P3 had higher Ω_2 values than their corresponding monomer EuVTPY, suggesting an increase of the covalence degree in the first coordination shell of Eu³⁺ ions and an enhancement of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ hypersensitive transition. This may also be due to the change of the chemical environment surrounding the Eu³⁺ ions, which was induced by the intra- and inter-molecular interactions between the EuVTPY unit and the neighboring chain consisting of PVK moieties. The higher values of Ω_4 for the Eu-polymers as compared with that of their corresponding monomer EuVTPY indicated a perturbation on the coordination effect of the ligands vinyl-tpy and TTA by the steric factors from the surrounding PVK units.

Table 1 Solid state and solution luminescence data of Eu-complexes											
Compound	In solid state						In THF solution				
	τ (ms)	$A_{\rm rad} \left({\rm s}^{-1} ight)$	I_{2}/I_{1}	η (%)	$\Omega_2 \ (10^{-20} \ { m cm}^2)$	$\Omega_4 \ (10^{-20} \ { m cm}^2)$	CIE	I_{2}/I_{1}	τ (ms)	Φ (%)	CIE
EuVTPY	0.63	595.28	11.35	37.92	15.04	1.71	0.67, 0.33	16.49	0.48	8.22	0.64, 0.31
P1	0.60	634.71	12.1	38.21	16.21	1.77	0.61, 0.30	12.47	0.49	1.31	0.31, 0.12
P2	0.63	673.02	12.54	42.49	17.35	1.74	0.66, 0.32	13.86	0.50	4.11	0.58, 0.28
P3	0.74	692.18	14.21	51.07	17.82	1.89	0.66, 0.33	14.08	0.56	8.59	0.60, 0.29

3.5 Electrochemical properties

The redox behavior of the monomer EuVTPY, P1, P2 and P3 is very important, as it can give information on the frontier orbitals of these compounds. In particular, by comparing with the monomer EuVTPY, the investigation is helpful to clearly understand the carrier migration between the PVK segments and EuVTPY moieties during the electroluminescent process. The electrochemical properties of EuVTPY, P1, P2 and P3 were investigated at 298 K in acetonitrile solutions versus the saturated calomel electrode (SCE) (Table 2 and Fig. 9). For monomer EuVTPY, one irreversible oxidation wave at 1.78 V was easily observed, which is attributed to the oxidation of terpyridyl moieties in vinyl-tpy. The corresponding half-wave potential $(V_{1/2}^{\text{oxd}})$ and onset potential $(V_{\text{onset}}^{\text{oxd}})$ are 1.60 and 1.23 V, respectively. According to the equation reported by de Leeuw et al.,²⁹ $E_{\text{LUMO}} = -(V_{\text{onset}}^{\text{red}} + 4.4 \text{ eV})$ and $E_{\text{HOMO}} = -(V_{\text{onset}}^{\text{oxd}} + 4.4 \text{ eV})$, in which E_{LUMO} is the energy level of the LUMO and E_{HOMO} is the energy level of the HOMO; E_{HOMO} of EuVTPY is about -5.63 eV. Meanwhile, for EuVTPY, two irreversible reduction waves at -1.24 and -1.57 V were observed. The former corresponds to the reduction of vinyl moieties in vinyl-tpy, and the latter should originate from its tpy moieties. Considering that after polymerization the vinyl moieties react to produce saturated ethenyl moieties, ELUMO of polymerized EuVTPY should be -3.01 eV corresponding to the second reduction peak.

For polymers P1, P2, and P3, two irreversible oxidations could be observed. The first irreversible oxidation wave was located 1.14, 1.12, and 1.16 V, and the second oxidation wave was located at 1.61, 1.65, and 1.59. The first irreversible oxidation wave is attributed to the oxidation of the tpy moieties, and the second is attributed to the carbazole moieties. In addition, due to the very low content of EuVTPY in these polymers, no distinct reduction peak is observed for P1, P2, and P3. According to their onset oxidation potentials, E_{HOMO} of **P1**, **P2** and **P3** is about -5.31 (5.67) eV. The energy gap between the LUMO and HOMO energy levels of P1, P2 and P3 is calculated to be 3.49 eV by reference to their absorption edge (carbazole moieties) of 355 nm. Thus, E_{LUMO} of **P1**, **P2** and **P3** is about -2.19 eV. **P1**, **P2** and P3 exhibit much stronger hole-injection ability but much weaker electron-injection ability than EuVTPY. Nevertheless, as the majority in the copolymers, PVK segments are dominant in carrier injection. The wrapping and embedment of Eu-complex segments in the nonconjugated systems would further enhance this situation. Therefore, this implies that under the electric field, firstly carriers are injected in PVK segments, then electrons can be captured by Eu-complex segments through intraand inter-chain carrier migration and finally holes hopping to the surrounding PVK segments can be attracted by



Fig. 9 CV cures of monomer EuVTPY and Eu-polymers measured in acetonitrile solution, containing 0.1 M Bu₄NClO₄ at 298 K. Scans rate 50 mV s⁻¹.

electronegative Eu-complex segments to form charge-transfer (CT) excitons.

3.6 Electroluminescence performance

In order to investigate the electroluminescence (EL) properties of the designed Eu-polymers, three types of spin-coated devices were fabricated to investigate the EL performance of **P1**, **P2** and **P3**. Devices A, B and C were single-layer PLEDs, and they were based on **P1**, **P2** and **P3** with the configuration of ITO/PEDOT (40 nm)/Eu-polymer (80 nm)/Ba (4 nm)/Al (120 nm). Devices D, E and F were double-layer PLEDs, and they were based on **P1**, **P2** and **P3** with the configuration of ITO/PEDOT (40 nm)/PVK (40 nm)/copolymer (80 nm)/Ba (3 nm)/Al (120 nm). Devices G and H were based on **P1** with the configuration of ITO/PEDOT (40 nm)/PVK (40 nm)/**P1**:OXD-7 (40% and 30%, 80 nm)/Ba (3 nm)/Al (120 nm).

EL spectra of the eight devices consist of the characteristic Eu^{3+} ion emission corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$ (j = 0-4) (Fig. 10). Moreover, the peaks at 580, 594, 653, and 697 nm are much weaker than those in the PL spectra in the solid state. Therefore, the main peak at 615 nm becomes more dominant as pure red emission, which exhibits extremely high color purity (CIE coordinates were around 0.66, 0.33) with a full width at halfmaximum of 10 nm. In particular, even at the highest voltage, EL spectra of devices A–H were still very stable. No distinct shortwavelength emission from PVK moieties was observed, which indicated that the efficient energy transfer from PVK segments to Eu(TTA)₃ moieties at the high current densities occurred.

Table 2 Electrochemical properties of monomer EuVTPY and Eu-polymers									
Compound	$V_{1/2}^{\mathrm{red}}(\mathrm{V})$	$V_{\text{onset}}^{\text{red}}(\mathbf{V})$	$V_{1/2}^{\text{oxd}}$ (V)	$V_{\text{onset}}^{\text{oxd}}(V)$	$E_{\rm HOMO}$ (eV)	E_{LUMO} (eV)			
EuVTPY	-1.06, -1.53	-0.91, -1.39	1.60	1.23	-5.63	-3.49, -3.01			
P1			1.07, 1.42	0.92, 1.28	-5.32, -5.68	-1.83, -2.19			
P2			1.06, 1.49	0.89, 1.26	-5.29, -5.66	-1.80, -2.17			
P3	—	—	1.09, 1.51	0.91, 1.31	-5.31, -5.71	-1.82, -2.22			

For single-layer PLEDs, the energy band diagram is shown schematically in Fig. 10(b). In the presence of ideal intramolecular energy transfer, electrons are preferentially injected from the Ba/Al cathode into the LUMO of the Eu-polymers P1, P2 and P3. Holes are injected from the ITO anode into the HOMO of the PEDOT, and then transported to the HOMO of P1, P2 and P3. With the subsequent recombination of holes and electrons in the Eu-polymers P1, P2 and P3, excitons are formed, and EL emission occurs. As show in Fig. 11, the turn-on voltage of A is 24 V at 1 cd m^{-2} , and its maximum brightness is 5.96 cd m^{-2} at 25.5 V with the current density of 178 mA cm⁻². Due to the maximum brightness of devices B and C being lower than 1 cd m^{-2} , we cannot define their turn-on voltage. The maximum brightnesses of B and C are 0.82 and 0.1 cd m^{-2} at 25.5 and 15.8 V with the current densities of 25.8 and 5.5 mA cm^{-2} , respectively. It is shown that the turn-on voltage of A is relatively high, and the maximum brightness of A is far higher than that of B and C. Moreover, the current density of A is much higher than those of B and C at the same voltages, and these results indicate that P1 exhibited much stronger carrier injection and transport ability than P2 and P3.30 The main reason might be that the majority of the Eu-polymers P1, P2 and P3 are the PVK segments, as is well known, which is an efficient hole transporting material, so the major carrier in devices A, B and C is hole carrier. The hole-injection ability of vinyl-tpy is much weaker than the PVK segments, thus, the hole-injection and transporting ability of the main chain is weakened upon increasing the content of vinyl-tpy. Although the electron injection ability of EuVTPY is much stronger than that of the PVK segments, because of the wrapping and embedment of the pendent EuVTPY moieties by the PVK segments, the improvement of electron injection and transporting upon increasing the content of EuVTPY from 0.73% to 3.69% is limited. Therefore, the carrier-injection and transporting in A is superior to that in B and C.

For single-layer PLEDs, we find the content of PVK segments is higher, and the maximum brightness and current density are much higher. This may be attributed to the fact that PVK is an

excellent hole transporting material, and upon increasing the content of PVK segments in the Eu-polymers, the hole-injection ability also increased, and more balanced carrier injection and transport can be obtained, so the properties of device A based on P1 as the emitting layer are superior to those of B and C. As mentioned above, one important problem can be raised. If we continued to increase the content of PVK in single-layer PLEDs, could the electroluminescence performances of corresponding PLEDs be further improved? To better confirm this idea, on the basis of single-layer devices A, B and C, we added one additional PVK layer (40 nm) and fabricated corresponding double-layer devices D, E and F, and the corresponding B-J-V and CE-J curves are shown in Fig. 12. After adding the PVK layer, the turnon voltage of D is increased to 27 V, but its maximum brightness improved to 18.9 cd m⁻² at 35.7 V with a current density of 81 mA cm⁻². Compared with the corresponding single-layer device A, although the turn-on voltage increased 3 V, the maximum brightness increased 3 times. Most importantly, due to the addition of the PVK layer, devices E and F had turn-on voltages of 25.7 and 38 V, respectively. The maximum brightness was 4.05 and 2.37 cd m⁻² at 33.0 and 38.5 V with current density of 18.9 and 25.8 mA cm⁻², respectively. Compared with the corresponding single-layer devices B and E, the maximum brightness increased nearly 5 and 24 times, respectively. As shown in Fig. 10(c), compared with single-layer PLEDs, although the channel of electron injection is not changed, the passage of holes from the ITO to emission layer Eu-polymer P1, P2 or P3 will be easier due to the existence of the hole transport layer PVK. Therefore the carrier-injection in D, E and F can be more balanced than in A, B and C, and more excitons can be formed with recombination in the emission layer. This is the reason why the electroluminescence performances of devices D, E and F are much better than those of A, B and C.

In particular, although the brightness–current density (B-J) curves of A, B, D and E show similar tendencies at the same current densities, the brightnesses of B and E are higher than those of A and D (Fig. S6 and S7†). This is very different from the doping devices, in which the brightness remarkably decreased



Fig. 10 EL spectra of the devices at their highest voltages and the schematic energy level diagram of the devices



along with an increase of the doping concentration. According to the EL spectra of A, B, D and E, the absence of the shortwavelength emission from PVK segments suggests the efficient exciton migration and Förster energy transfer in both Eu-polymers P1 and P2. If the EL process of A, B, D and E mainly involves these two channels, due to the Eu-chelated units in device B (E) being higher than that of A (D), B (E) should have much higher brightness than that of A (D) at the same current density. However, the brightness of A (D) is higher than that of B (E) because of the worse concentration guenching of P2. According to electrochemical analysis, the LUMO energy levels of the PVK segments and Eu-chelated segments are -2.0 and -3.5 eV, respectively. Thus, the Eu-chelated repeating units introduce electron traps with a depth of as much as 1.5 eV, which makes the electron capture efficient. Thus, after electrons are trapped in Eu-chelated segments, the surrounding holes would be attracted by the coulomb force to form charge transform (CT) excitons. Obviously, P2 with the higher Eu-chelated content could form more excitons than P1, and finally realize the higher EL brightness at the same current density. This implies that for devices A, B, D and E, the carrier trapping might be the main channel involved in the EL process.³¹

After adding an additional PVK layer, although the EL performances of double-layer D, E and F are much better than

those of corresponding single-layer A, B and C, the maximum brightness and efficiency of the PLEDS are relatively low. In addition, the above mentioned results show that the difficulty of electron injection and transporting is the main reason for the low brightness of A to F. In order to improve the electron injection and preserve the advantage of the good hole injection, an excellent electron transport material OXD-7 was blended in the emitting layer. Due to the EL performances of devices A and D based on P1 as the emitting layer being the best among the devices, we next chose P1 as the emitting layer, OXD-7 (electron transport material) as blend material, and PVK as hole transport material to fabricate two novel PLEDs. The configuration of the devices was ITO/PEDOT (40 nm)/PVK (40 nm)/P1: OXD-7 (40%, and 30%, 80 nm)/Ba (3 nm)/Al (120 nm). The LUMO level of OXD-7 is -2.8 eV, which is close to the vacuum level of Ba/Al of -2.7 eV (Fig. 10(d)). It is shown that the turn-on voltage of G is remarkably reduced from 27 V to 17 V, and its maximum brightness of 68.2 cd m⁻² is achieved at 23.5 V with the current density of 88.7 mA cm⁻². H had a turn-on voltage of 20 V. The maximum brightness of H was 35.4 cd m^{-2} at 28.0 V with the current density of 69.8 mA cm⁻² (Fig. 13). Compared with the corresponding undoped device D, the turn-on voltages of G and H were much lower because of their improved electron injection and transporting. The maximum brightnesses of G



Fig. 12 Left: brightness-current density-voltage (B-J-V) curves of devices D-F. Right: CE-current density (CE-J) curves of devices D-F.

and H were improved 3.6 and 1.9 times, respectively. It is noteworthy that the turn-on voltage decreased from 20 to 17 V with increasing doping content of OXD-7 from 30 wt% for device H to 40 wt% for device G. This result indicates that the doping devices G and H mainly operate by the carrier-trapping mechanism. The reason for the better EL performance of device G or H can be attributed to the fact that the electron can be easily injected in the emitting layers after blending the electron transporting material OXD-7. The increasing concentration of electrons greatly facilitates the formation of excitons. In addition, with the content of OXD-7 increasing, although parts of the excitons were still formed by carrier-trapping, most of the excitons were formed at PVK segments, then, the energy trans-

tion, with the content of OXD-7 increasing, although parts of the excitons were still formed by carrier-trapping, most of the excitons were formed at PVK segments, then, the energy transfers to Eu-chelated segments through exciton migration and Förster energy transfer. For these reasons, the EL properties of device G with a high content of OXD-7 (40 wt%) are better than those of device H with a low content of OXD-7 (30 wt%). The EL efficiencies of A–H, except B and C, were also calcu-

lated. Their current efficiency (CE)-J curves are shown in Fig. 11–13. The maximum CE of A was 0.0036 cd A^{-1} at 167.99 mA cm $^{-2}$, corresponding to the power efficiency (PE) of 0.0017 Im W^{-1} and EQE (external quantum efficiency) of 0.0067%. After adding one PVK layer, the maximum efficiency of D was greatly improved to 0.023 cd A^{-1} , 0.021 lm W^{-1} , and 0.009% at 57 mA cm⁻². Meanwhile, devices E and F had maximum CE of 0.031 and 0.0091 cd A^{-1} at 8.67 and 25.8 mA cm⁻², corresponding to 0.003 and 7.5 \times 10^{-4} Im $\text{W}^{-1}\text{,}$ and 0.012 and 0.004%, respectively (Fig. 12). Compared with corresponding single-layer device A (P1 as emitting layer), the CE, PE and EQE of the double-layer device D increased 6, 12 and 1.3 times, and the results indicated that introducing the additional PVK layer into single-layer Eu-polymer PLEDs is very efficient for improving the EL performances. To the best of our knowledge, this is the first report in which the EL properties of these PLEDs could be modified by adding an additional PVK layer into Eupolymers. After blending the electron transport material OXD-7 with P1, the EL efficiency of G (OXD-7 content: 40%) was greatly improved to 0.18 cd A^{-1} , 0.031 lm W^{-1} , and 0.37% at 9.5 mA cm^{-2} (Fig. 13). Meanwhile, H had the maximum CE of 0.12 cd

Paper

 A^{-1} at 6.8 mA cm⁻², corresponding to 0.018 lm W⁻¹, and 0.24%. Obviously, the more balanced carrier injection and transporting in G and H was effective in improving the device efficiencies. Compared with single-layer device A, for device G, the CE, PE and EQE increased 53, 18, and 55 times, respectively, and for device H, the CE, PE and EQE increased 35, 10.5, and 36 times, respectively. It is noteworthy that the EL efficiencies of the devices do not drop remarkably when the current density is increased (Fig. 13), and when the current density reaches its maximum, the devices still maintain a relatively high value. This is very different to the devices based on pure small molecule Eu-complexes or Eu-containing doping systems, whose efficiencies greatly decrease along with an increase of the current density. Therefore, this indicates that in P1, P2 and P3 the uniform dispersion of the emissive Eu³⁺ chelate moieties in the host matrix through covalent bonds can efficiently restrain the concentration guenching and T-T annihilation even at the highest exciton concentrations.32 It is also noted that although P2 and P3 have higher PL quantum efficiency in solid than P1, the devices based on P1 exhibit much higher efficiencies than those based on P2 and P3. This should be attributed to the different emission mechanisms of PL and EL. The multiparticle quenching effect is much more dominant and effective in the EL process than in the PL process. Therefore, the higher Eu³⁺ content may facilitate the interaction between the segments and consequently reduce the EL efficiencies by those quenching effects.

The EL performances from several recent representative reports about Eu-polymers are listed in Table 3. The EL performance of device G with PVK as a hole transport material, and OXD-7 (40 wt%) as the electron transport material compares favorably with these results. The maximum brightness, PE and CE of G is the third-best reported, and the EQE is the second-best reported so far. These excellent performances originate from the good comprehensive properties of **P1** in intra- and interchain energy transfer, high PL efficiencies, stable structure and efficient mitigation of concentration quenching and T–T annihilation. Although the EL performances of G are not the highest among the reported



Fig. 13 Left: brightness-current density-voltage (B-J-V) curves of devices G-H. Right: CE-current density (CE-J) curves of devices G-H.

Paper

Eu-containing copolymers, to the best of our knowledge, this is the first example of electroluminescent diodes based on Eucomplexes as emitting layers with tpy as a neutral ligand. These results illustrate the potential application of polymerizable tpy ligands in high performance EL Eu-chelated polymers. However, the EL performance based on **P1**, **P2** and **P3** as the emission layer is still inferior to those of small molecular Eucomplexes as the emission layer, which may be attributed to the simple configuration of devices fabricated through spin coating, the possibility of reversible energy transfer between Eucomplexed moieties and PVK segments, and the different emission mechanism of PL and EL. Through the device optimization, the EL performance of **P1**, **P2** and **P3** would be further improved.

4 Conclusions

In this work, we have designed and synthesized three nearly monochromatic red electroluminescent chelating polymers containing carbazole segments and tpy moieties which serve as neutral ligands to coordinate with the Eu(TTA)₃ complex. The resulting copolymers exhibited good solubility, as well as good thermal stability and high glass transition temperatures. Our investigations showed that the functional tpy ligand and the corresponding Eu-chelate segments significantly improve the properties of the Eu-complex nonconjugated copolymers. It is shown that the strong coordination ability of tridentate tpy ligands facilitates the stability of the complex monomer during polymerization. P1, P2 and P3 exhibit enhanced emission from Eu³⁺ ions and high PL quantum efficiency in solid of 40%, which implies the efficient intra- and inter-chain energy transfer in P1, P2 and P3. The pure-red emission from the devices of P1, P2 and P3 was demonstrated. Favorable EL performance including a relatively low turn-on voltage of 17 V and maximum brightness of 68.2 cd m⁻² were realized. To the best of knowledge, this is the first report of the EL performance of Eucomplexes based on tpy as a neutral ligand. Our results demonstrate the potential application of polymerizable tpy ligands in high performance EL europium-complex polymers. The further purposeful chemical modification of tpy ligands is ongoing in our group. It has been shown that the suitable excited energy levels of tpy ligands have a strong effect on the intra-chain energy transfer and charge trapping is one of the most important channels in the EL process. Through introducing different functional groups, the excited energy levels and

the frontier orbital levels of the tpy ligands can be conveniently tuned, so that lower turn-on voltage, higher brightness and higher efficiency can be obtained.

Acknowledgements

The authors appreciate the Guangdong-Hongkong Technology Cooperation Funding (Project no. 2009A091300012) and National Natural Science Foundation of China (Project no. 20974121).

Notes and references

- 1 (a) M. J. Park, J. H. Lee, J. H. Kwak, I. H. Jung, J. H. Park, H. Y. Kong, C. H. Lee, D. H. Hwang and H. K. Shim, *Macromolecules*, 2009, 42, 5551–5557; (b) G. R. Whittell, M. D. Hager, U. S. Schubert and I. Manners, *Nat. Mater.*, 2011, 10, 176–188; (c) J. X. Jiang, C. Y. Jiang, W. Yang, H. Y. Zhen, F. Huang and Y. Cao, *Macromolecules*, 2005, 38, 4072–4080; (d) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, 347, 539–541; (e) S. Basak, Y. S. L. V. Narayana, M. Baumgarten, K. Müllen and R. Chandrasekar, *Macromolecules*, 2013, 46, 362–369.
- 2 (a) A. Bandyopadhyay, S. Sahu and M. Higuchi, J. Am. Chem. Soc., 2011, 133, 1168–1171; (b) Q. D. Ling, Y. Song, S. J. Ding, C. X. Zhu, D. S. H. Chan, D. L. Kwong, E. T. Kang and K. G. Neoh, Adv. Mater., 2005, 17, 455–459; (c) B. Korybut-Daszkiewicz, R. Bilewicz and K. Wozniak, Coord. Chem. Rev., 2010, 254, 1637–1660; (d) M. J. Cho, D. H. Choi, A. Sullivan, A. J. P. Akelaitis and L. R. Dalton, Prog. Polym. Sci., 2008, 33, 1013–1058; (e) Q. D. Ling, D. J. Liaw, C. X. Zhu, D. S. H. Chan, E. T. Kang and K. G. Neoh, Prog. Polym. Sci., 2008, 33, 917–978; (f) X. Y. Chen, X. P. Yang and B. J. Holliday, J. Am. Chem. Soc., 2008, 130, 1546–1547; (g) Z. M. Liu, A. A. Yasseri, J. S. Lindsey and D. F. Bocian, Science, 2003, 302, 1543–1545.
- 3 (a) I. Radivojevic, A. Varotto, C. Farley and C. M. Drain, Energy Environ. Sci., 2010, 3, 1897–1909; (b) Y. Li,
 Y. Z. Bian, M. Yan, P. S. Thapaliya, D. Johns, X. Z. Yan,
 D. Galipeau and J. Z. Jiang, J. Mater. Chem., 2011, 21, 11131–11141; (c) M. Jurow, A. E. Schuckman, J. D. Batteas and C. M. Drain, Coord. Chem. Rev., 2010, 254, 2297–2310; (d) C. M. Yan, Y. P. Fan and D. H. Zhao, Macromolecules,

Table 3 EL performances of the Eu-containing polymers								
		Max. brightness (cd m^{-2})	Max. EL efficiency					
Reference	(V)		$CE (cd A^{-1})$	$PE (lm W^{-1})$	EQE (%)			
30(a)	17	16.4	_	$0.247 \ (6.29 \ cd \ m^{-2})$	_			
30(b)	30	46		$0.035 (9.8 \text{ cd m}^{-2})$	_			
31(a)	13	36.9	$0.035 (21.5 \text{ cd } \text{m}^{-2})$	$0.0073 (21.5 \text{ cd m}^{-2})$	$0.037 (21.5 \text{ cd } \text{m}^{-2})$			
31(b)	12.5	149.1	$0.41 (71.6 \text{ cd m}^{-2})$	$0.089 (71.6 \text{ cd m}^{-2})$	$0.43 (71.6 \text{ cd m}^{-2})$			
32	8	126	0.52 (1 cd m ⁻²)		· · · ·			
Device G of this work	17	68.2	$0.18 (9.5 \text{ cd m}^{-2})$	$0.031 (15.7 \text{ cd } \text{m}^{-2})$	$0.37 (9.5 \text{ cd } \text{m}^{-2})$			

2012, 45, 133–141; (e) P. T. Wu, T. Bull, F. S. Kim, C. K. Luscombe and S. A. Jenekhe, *Macromolecules*, 2009, 42, 671–681.

- 4 X. H. Yang, D. C. Muller, D. Neher and K. Meerholz, *Adv. Mater.*, 2006, **18**, 948–954.
- 5 (a) M. J. Park, J. H. Lee, J. H. Kwak, I. H. Jung, J. H. Park and H. Y. Kong, *Macromolecules*, 2009, 42, 5551–5557; (b) A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby and A. Köhler, *J. Am. Chem. Soc.*, 2004, 126, 7041–7048; (c) P. I. Lee and S. L. C. Hsu, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, 45, 1492–1498; (d) X. Chen, J. L. Liao, Y. Liang, M. O. Ahmed, H. E. Tseng and S. A. Chen, *J. Am. Chem. Soc.*, 2003, 125, 636–637.
- 6 (a) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, Chem. Rev., 2009, 10897-10915; (b) C. Coluccini, A. K. Sharma, D. Merli, D. V. Griend, B. Mannucci and D. Pasini, Dalton Trans., 2011, 40, 11719-11725; (c) C. Coluccini, P. Metrangolo, M. Parachini, D. Pasini, G. Resnati and P. Righetti, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 5202-5213; (d) S. F. Li, G. Y. Zhong, W. H. Zhu, F. Y. Li, J. F. Pan, W. Huang and H. Tian, J. Mater. Chem., 2005, 15, 3221-3228; (e) G. Zucchi, T. Jeon, D. Tondelier, D. Aldakov, P. Thuery, M. Ephritikhine and B. Geffroy, J. Mater. Chem., 2010, 20, 2114-2120; (f) P. Lenaerts, A. Storms, J. Mullens, J. D'Haen, C. Gorller-Walrand, K. Binnemans and K. Driesen, Chem. Mater., 2005, 17, 5194-5201; (g) D. Pasini, P. P. Righetti and V. Rossi, Org. Lett., 2002, 4, 23-26; (h) C. Coluccini, A. K. Sharma, M. Caricato, A. Sironi, E. Cariati, S. Righetto, E. Tordin, C. Botta, A. Forni and D. Pasini, Phys. Chem. Chem. Phys., 2013, 15, 1666-1674.
- 7 (a) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, 102, 2357–2368; (b) S. V. Eliseeva and J. C. G. Bunzli, *Chem. Soc. Rev.*, 2010, 39, 189–227.
- 8 C. Adachi, M. A. Baldo and S. R. Forrest, *J. Appl. Phys.*, 2000, **87**, 8049–8055.
- 9 J. Kido, H. Hayase, K. Hongawa, K. Nagai and K. Okuyama, *Appl. Phys. Lett.*, 1994, **65**, 2124–2126.
- 10 T. X. Li, H. Fukuyama, Y. Yamagata, H. L. Lan and J. Kido, *Polym. Adv. Technol.*, 2004, **15**, 302–305.
- 11 H. Xu, K. Yin and W. Huang, *Chem.–Eur. J.*, 2007, **13**, 10281–10293.
- 12 (a) J. Pei, L. X. Liu, L. W. Yu, Y. H. Lai, Y. H. Niu and Y. Cao, Macromolecules, 2002, 35, 7274–7280; (b) Q. D. Ling, E. T. Kang, K. G. Neoh and W. Huang, Macromolecules, 2003, 36, 6995–7003; (c) P. Lenaerts, K. Driesen, D. R. Van and K. Binnemans, Chem. Mater., 2005, 17, 2148–2154; (d) Q. D. Ling, W. Wang, Y. Song, C. X. Zhu, D. S. H. Chan and E. T. Kang, J. Phys. Chem.B, 2006, 110, 23995–24001; (e) A. Balamurugan, M. L. P. Reddy and M. Jayakannan, J. Phys. Chem. B, 2009, 113, 14128–14138.
- 13 (a) M. J. Yang, Q. D. Ling, M. Hiller, X. Z. Fun, X. Liu and L. H. Wang, J. Polym. Sci., Part A: Polym. Chem., 2000, 38, 3405–3411; (b) Y. X. Cheng, X. W. Zou, D. Zhu, T. S. Zhu, Y. Liu and S. W. Zhang, J. Polym. Sci., Part A: Polym. Chem., 2007, 45, 650–660; (c) G. A. Wen, X. R. Zhu, L. H. Wang, J. C. Feng, R. Zhu and W. Wei, J. Polym. Sci., Part A: Polym.

Chem., 2007, 45, 388–394; (d) Z. G. Zhang, J. B. Yuan, H. J. Tang, H. Tang, L. N. Wang and K. L. Zhang, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 210–221.

- 14 (a) W. Andreas, W. Andreas, F. Schlutterand and U. S. Schubert, Chem. Soc. Rev., 2011, 40, 1459-1511; (b) P. P. Kumar, G. Premaladha and B. G. Maiya, Chem. Commun., 2005, 3823-3825; (*c*) М. Licini and J. A. G. Williams, Chem. Commun., 1999, 1943-1944; (d) P. P. Laine, F. Loiseau, S. Campagna, I. Ciofini and C. Adamo, Inorg. Chem., 2006, 45, 5538-5551; (e) P. P. Laine, S. Campagna and F. Loiseau, Coord. Chem. *Rev.*, 2008, 252, 2552–2571; (f) H. Hofmeier and U. S. Schubert, Chem. Soc. Rev., 2004, 33, 373-399.
- 15 (a) O. Kotova, R. Daly, C. M. G. dos Santos, M. Boese, P. E. Kruger, J. J. Boland and T. Gunnlaugsson, Angew. Chem., Int. Ed., 2012, 51, 7208–7212; (b) W. S. Lo, W. M. Kwok, G. L. Law, C. T. Yeung, C. T. L. Chan, H. L. Yeung, H. K. Kong, C. H. Chen, M. B. Murphy, K. L. Wong and W. T. Wong, Inorg. Chem., 2011, 50, 5309– 5311; (c) R. Shunmugam and G. N. Tew, J. Am. Chem. Soc., 2005, 127, 13567–13572; (d) B. Song, G. L. Wang, M. Q. Tan and J. L. Yuan, J. Am. Chem. Soc., 2006, 128, 13442–13450; (e) J. Costa, R. Ruloff, L. Burai, L. Helm and A. E. Merbach, J. Am. Chem. Soc., 2005, 127, 5147–5157; (f) N. Chandrasekhar and R. Chandrasekar, J. Org. Chem., 2010, 75, 4852–4855.
- 16 L. Matthews and E. T. Knobbe, *Chem. Mater.*, 1993, 5, 1697–1700.
- 17 J. J. P. Stewart, MOPAC 2012 Manual, Stewart Computational Chemistry, Colorado Springs, 2012.
- 18 (a) A. P. Souza, F. A. A. Paz, R. O. Freire, L. D. Carlos,
 O. L. Malta, S. A. Junior and G. F. de Sa, *J. Phys. Chem. B*,
 2007, 111, 9228–9238; (b) O. Freire, G. B. Rocha and
 A. M. Simas, *Inorg. Chem.*, 2005, 44, 3299–3310.
- 19 (a) D. P. Li, C. H. Li, J. Wang, L. C. Kang, T. Wu, Y. Z. Li and X. Z. You, *Eur. J. Inorg. Chem.*, 2009, 4844–4849; (b) X. L. Li, F. R. Dai, L. Y. Zhang, Y. M. Zhu, Q. Peng and Z. N. Chen, *Organometallics*, 2007, 26, 4483–4490.
- 20 B. W. Wang, S. D. Jiang, X. T. Wang and S. Gao, *Sci. China*, *Ser. B: Chem.*, 2009, **52**, 1739–1758.
- 21 J. H. Wang and G. S. Hanan, Synlett, 2005, 8, 1251-1254.
- 22 A. Karali, P. Dais, E. Mikros and F. Heatley, *Macromolecules*, 2001, 34, 5547–5554.
- 23 A. Karali, G. E. Froudakis, P. Dais and F. Heatley, *Macromolecules*, 2000, **33**, 3180–3183.
- 24 (a) R. Feng, F. L. Jiang, M. Y. Wu, L. Chen, C. F. Yan and M. C. Hong, *Cryst. Growth Des.*, 2010, 10, 2306–2313; (b)
 Y. J. Li and B. Yan, *Dalton Trans.*, 2010, 39, 2554–2562; (c)
 C. L. Yang, J. X. Luo, J. Y. Ma, M. G. Lu, L. Y. Liang and B. H. Tong, *Dyes Pigm.*, 2011, 92, 696–704.
- 25 (a) A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans.* 2, 1999, 493–504; (b) C. L. Yang, J. Xu, J. Y. Ma, D. Y. Zhu, Y. F. Zhang, L. Y. Liang and M. G. Lu, *Photochem. Photobiol. Sci.*, 2013, 12, 330–338.
- 26 W. H. Melhuish, J. Phys. Chem., 1961, 65, 229-235.

- 27 (*a*) R. Ferreira, P. Pires, B. D. Castro, R. A. Sa Ferreira, L. D. Carlos and U. Pischel, *New J. Chem.*, 2004, 28, 1506–1513; (*b*) C. L. Yang, J. Xu, R. Zhang, Y. F. Zhang, Z. X. Li, Y. W. Li, L. Y. Liang and M. G. Lu, *Sens. Actuators, B*, 2013, 177, 437–444.
- 28 (a) M. H. V. Werts, R. T. F. Jukes and J. W. Verhoeven, *Phys. Chem. Chem. Phys.*, 2002, 4, 1542–1548; (b) H. Liang and F. Xie, *Spectrochim. Acta, Part A*, 2010, 75, 1191–1914.
- 29 D. M. de Leeuw, M. M. J. Simenon, A. R. Brown and R. E. F. Einerhand, *Synth. Met.*, 1997, **87**, 53–59.
- 30 (a) M. J. Yang, Q. D. Ling, M. Hiller, X. Z. Fun, X. Liu, L. H. Wang and W. G. Zhang, J. Polym. Sci., Part A: Polym.

Chem., 2000, **38**, 3405–3411; (*b*) Z. G. Zhang, J. B. Yuan, H. J. Tang, H. Tang, L. N. Wang and K. L. Zhang, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 210–221.

- 31 (a) H. Xu, R. Zhu, P. Zhao, L. H. Xie and W. Huang, *Polymer*, 2011, 52, 804–813; (b) H. Xu, R. Zhu, P. Zhao and W. Huang, *J. Phys. Chem. C*, 2011, 115, 15627–15638.
- 32 Q. D. Ling, Q. J. Cai, E. T. Kang, K. G. Neoh, F. R. Zhu and W. Huang, *J. Mater. Chem.*, 2004, **14**, 2741–2748.
- 33 A. Pacini, M. Caricato, S. Ferrari, D. Capsoni, A. M. de Ilarduya, S. Munoz-Guerra and D. Pasini, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4790–4799.