Organic & Biomolecular Chemistry

Cite this: Org. Biomol. Chem., 2012, 10, 8701

www.rsc.org/obc



Synthesis and photophysical properties of phosphorus(v) porphyrins functionalized with axial carbazolylvinylnaphthalimides[†]

Yong Zhan,^a Kaiyu Cao,^a Chenguang Wang,^a Junhui Jia,^a Pengchong Xue,^a Xingliang Liu,^a Xuemei Duan^b and Ran Lu^{*a}

Received 28th July 2012, Accepted 12th September 2012 DOI: 10.1039/c2ob26478a

We have synthesized new D-A-D type phosphorus(v) porphyrin derivatives 1 and 2 functionalized with axial carbazolylvinylnaphthalimide units. The absorption bands of the obtained phosphorus(v) porphyrins were in the range 250–640 nm with high molar absorption coefficients, meaning strong light-harvesting abilities. Notably, it is found that the devices based on phosphorus(v) porphyrins with a configuration structure of [ITO/PEDOT : PSS/organic active film/LiF/A1] give an incident-photon-to-current conversion efficiency (IPCE) response. The maximal IPCE value reaches 2.76% for the device based on compound 2, which is much higher than that of 0.20% for compound 1. The reason might be due to the low oxidation potential and the strong light-harvesting ability of the enlarged conjugation of the axial units in compound 2. Therefore, we deduced that photo-induced electron transfer happened in phosphorus(v) porphyrins bearing axial conjugated donor units, which would make them good candidates for photovoltaic materials that could be applied in solar cells.

Introduction

In recent years, various conjugated porphyrins have been widely employed as building blocks for photo-active and electro-active materials due to their excellent light-harvesting abilities and potential applications in molecular electronics, photochemical energy conversion and storage.¹⁻³ In order to realize artificial molecular systems for photoenergy conversion and photoelectronic operation, natural photosynthesis systems are very useful examples, and various mimetic systems containing porphyrins have been synthesized.⁴⁻⁶ So far most of the porphyrin arrays reported have been synthesized via typical organic reaction sequences carried out at meso- or/and β-positions in porphyrin rings.⁷⁻¹³ However, less attention has been paid to an "axial covalent bonding" strategy in fabricating functional porphyrins, although novel photoelectric properties and functionalities would be afforded when the conjugated groups are attached to the axial positions of the porphyrin ring. It has been known

that dichloride 5,10,15,20-tetraphenyl phosphorus(v) porphyrin $[P(TPP)Cl_2]^+$ is an axial-bonding block, in which the phosphorus(v) porphyrin core is a strong electron acceptor and the P-Cl bonds are reactive toward phenols and alcohols.¹⁴ Therefore, the central phosphorus atom could be connected to desired conjugated moieties in order to construct novel porphyrin arrays. For example, Segawa and co-workers reported the competition between photo-induced energy transfer and electron transfer from an excited pyrene to the phosphorus(v) porphyrin core.¹⁵ Maiya and co-workers have investigated the intramolecular electron and energy transfer processes in D-A type phosphorus(v) porphyrins.¹⁶ Our group has prepared phosphorus(v) porphyrins bearing carbazole-based dendrons in axial positions, which are nonfluorescent due to the electron transfer from dendritic carbazoles to the phosphorus(v) porphyrin core.17 However, the absorption of the oligocarbazole is located in the high-energy region,^{18,19} which would limit its light-harvesting ability towards most visible light. In order to enlarge the absorption wavelength range of phosphorus(v) porphyrins, herein, naphthalimide units are introduced as the linker between carbazole and phosphorus(v) porphyrin. In this work, new D-A-D type phosphorus(v) porphyrins 1 and 2 (Chart 1) with strong light-harvesting abilities have been synthesized. It is interesting that the device based on phosphorus(v) porphyrin 2 with a configuration structure of [ITO/PEDOT: PSS/organic active film/LiF/A1] gives an obvious incident-photon-to-current conversion efficiency (IPCE) response to the visible light. We suggested that photo-induced electron transfer occurred in the synthesized phosphorus(v) porphyrins bearing axial conjugated donor units, which would

^aState Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: luran@mail.jlu.edu.cn; Fax: +86-431-88923907; Tel: +86-431-88499179

^bState Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130021, P. R. China

[†]Electronic supplementary information (ESI) available: UV-vis absorption and fluorescence spectra; cyclic voltammetry diagrams; ¹H NMR, ¹³C NMR, and MALDI/TOF MS spectra of new compounds. See DOI: 10.1039/c2ob26478a



Chart 1 The molecular structures of phosphorus(v) porphyrins 1 and 2.

make them become good candidates for photovoltaic materials that could be applied in solar cells.

Result and discussion

Synthesis and characterizations

The synthetic routes for phosphorus(v) porphyrins functionalized with axial carbazolylvinylnaphthalimides (1 and 2) are sketched in Schemes 1 and 2. Firstly, 9-octyl-9*H*-carbazole-3-carbalde-hyde (3) was prepared from 9-octyl-9*H*-carbazole under Vilsmeier reaction condition,^{20a} and the iodination of compound 3 gave 6-iodo-9-octyl-9*H*-carbazole-3-carbaldehyde (4).^{20b} Meanwhile, compound 3 was transformed into 9-octyl-3-vinyl-9*H*-carbazole (5) *via* Wittig reaction with methyltriphenylphosphoniumiodine in a yield of 90%.^{20c} Then, the Heck reaction between compounds 4 and 5 afforded compound 6, catalyzed by Pd(OAc)₂ at 110 °C for 12 h in a yield of 76%.²¹ Similarly, compound 7 was obtained through a Wittig reaction between compound 6 and methyltriphenylphosphoniumiodine in a yield of 78%. After that, compounds 8 and 9 with methoxy terminal groups were generated from compounds 5 and 7, respectively, by Heck reactions with 4-bromo-N-(4'-methoxyphenyl)-1,8naphthalimide²² in yields of 72% and 65%.²³ The precursors 10 and 11 for the syntheses of phosphorus(v) porphyrin derivatives 1 and 2 were easily prepared from compounds 8 and 9, respectively, by the cleavage of methoxy in the presence of tribromoborane at -78 °C in dry dichloromethane in yields of 92% and 65%.24a Finally, the nucleophilic substitution reactions of the phenols 10 and 11 with dichloride 5,10,15,20-tetraphenyl phosphorus(v) porphyrin^{24b-e} in dry pyridine afforded phosphorus(v) porphyrins functionalized with axial carbazolylvinylnaphthalimides 1 and 2 in yields of 71% and 60%.²⁵ Similarly, reference compound 12 was prepared from phenol and dichloride 5.10.15.20-tetraphenyl phosphorus(v) porphyrin in dry pyridine.²⁶ All the intermediates and the final products were purified by column chromatography, and the new compounds were characterized with FT-IR, ¹H NMR, ¹³C NMR, elemental analysis, and MALDI/TOF mass or HRMS spectroscopy. From the FT-IR spectra of the compounds 1, 2, 8-11, we could find the vibration absorption bands appeared at *ca*. 960 cm^{-1} arising from the wagging vibration of the *trans*-double bond (CH=CH), and the bands at ca. 860 cm⁻¹ for compounds 1 and 2 were ascribed to the wagging vibration of P-O. In addition, the



Scheme 1 Syntheses of carbazolylvinylnaphthalimides 10 and 11. (a) POCl₃, DMF, ClCH₂CH₂Cl, reflux; (b) KI, KIO₃, AcOH, 80 °C; (c) $[Ph_3PCH_3]^+I^-$, *t*-BuOK, THF, 0 °C to rt; (d) Pd(OAc)₂, K₂CO₃, DMF, Bu₄NBr, 110 °C; (e) BBr₃, CH₂Cl₂, -78 °C to rt.



Scheme 2 Syntheses of phosphorus(v) porphyrins 1, 2 and 12.

¹H NMR spectra of compounds **1** and **2** also confirmed that the vinyl groups adopted the *trans*-conformation on account of the absence of the signal at ~6.5 ppm assigned to the proton in the *cis*-double bond (CH=CH).^{27,28} On the other hand, the disappearance of the internal H signal of the porphyrin rings indicated the formation of the phosphorus(v) porphyrins. The obtained phosphorus(v) porphyrins **1** and **2** were readily dissolved in common organic solvents, including dichloromethane, chloroform, toluene, tetrahydrofuran, *etc*.

UV-vis absorption and fluorescent spectra

The normalized UV-vis absorption spectra of the phosphorus(v) porphyrins **1**, **2** and **12** in chloroform are shown in Fig. 1 and the data are listed in Table S1 (ESI[†]). We can find two Q-bands at *ca*. 564 nm and 610 nm for compounds **1** and **2**, which are similar to those of the reference compound **12**, suggesting the formation of phosphorus(v) porphyrins.^{29a} In addition, the Soret bands for compounds **1**, **2** and **12** appear at *ca*. 440 nm. The



Fig. 1 Normalized UV-vis absorption spectra of the phosphorus(v) porphyrins 1, 2 and 12 in chloroform $(5.0 \times 10^{-6} \text{ M})$.

obvious absorptions in the range of 300-400 nm for compounds 1 and 2 compared with the very weak ones for compound 12^{29b} mainly originate from the units of carbazolylvinylnaphthalimides. The other absorption bands in the range of 460-540 nm for compounds 1 and 2 are due to the intramolecular charge transfer (ICT) transition from carbazole to naphthalimide in the axial positions of the phosphorus(v) porphyrins, which can be confirmed by the solvent-dependent absorption and fluorescent emission spectra of compound 8, the axial-functionalized moiety in compound 1. As shown in Fig. S1 (see ESI⁺), it is clear that the absorption band of compound 8 at ca. 420 nm in hexane redshifts with increasing the polarity of the solvents, and reaches ca. 455 nm in DMF. On the other hand, in the nonpolar solvents, such as hexane and cyclohexane, the fluorescence spectra of compound 8 give vibration structures, and the maximal emission bands are located at ca. 485 nm. As the polarity of the solvents increases, the emission band becomes broader and obviously red-shifts, for instance, the emission red-shifts to ca. 650 nm in DMF. Therefore, it indicates an intramolecular charge-transfer (ICT) character for the excited state of the axial-functionalized moieties in the synthesized phosphorus(v) porphyrins.^{29c} Notably, the synthesized phosphorus(v) porphyrins 1 and 2 show several absorption bands in the range 250-640 nm with high molar absorption coefficients (Table S1^{\dagger}, for example, ε (M⁻¹ cm^{-1}) = 7.69 × 10⁴ for 300 nm, 8.20 × 10⁴ for 350 nm, 1.66 × 10^5 for 440 nm), meaning strong light-harvesting abilities, which is of importance in photovoltaic materials. In addition, we can find from Fig. S2a⁺ that the UV-vis absorption spectrum for compound 1 can be regarded as the superposition of the ones of compounds 8 and 12. Similar absorption spectral behavior can also be detected for compound 2 (Fig. S2b[†]). It indicates that the electronic coupling between the axial substituted chromophores and the phosphorus(v) porphyrin cores in compounds 1 and 2 in the ground state should be neglected. Notably, there is no distinct shift of the Soret and Q bands of compounds 1 and 2 compared with those of 12, meaning that the electronic structures of the phosphorus(v) porphyrin cores may not change with increasing the conjugation of the axial functional groups. The absorption spectra of 1 and 2 in the films obtained through spinning the chloroform solutions (2.0 \times 10⁻³ M) onto quartz slides are



Fig. 2 Fluorescence emission spectra of the phosphorus(v) porphyrins 1, 2 and 12 in CHCl₃ (5.0×10^{-6} M, $\lambda_{ex} = 570$ nm).

shown in Fig. S3 (see ESI⁺). It is clear that the Soret bands of compounds 1 and 2 in the films red-shift to 450 nm and 448 nm, respectively, from 440 nm in chloroform, which might be due to the aggregation in the solid state. The smaller red-shift of the Soret band in compound 2 compared with that in compound 1 might result from a larger site-isolation effect of the more extended conjugated carbazolylvinylene units on the porphyrin core.³⁰

Fig. 2 shows the fluorescence emission spectra of 1, 2 and 12 in CHCl₃ (5.0 \times 10⁻⁶ M). When excited at 570 nm, which can selectively excite the phosphorus(v) porphyrin core instead of the carbazolylvinylnaphthalimide units, compound 12 gives strong emission at 618 nm and 669 nm. However, the emission at ca. 619 nm and ca. 670 nm coming from the phosphorus(v) porphyrin cores in compounds 1 and 2 at the same concentration is obviously weaker than that of compound 12, suggesting that the attachment of carbazolylvinylnaphthalimides to the axial positions of phosphorus(v) porphyrins might impart a fast deactivation of the porphyrin's singlet excited state through electron transfer,³¹ which will be discussed below.

Molecular orbital calculations

The frontier orbital plots of the highest occupied molecular orbital (HOMO and HOMO -1) and the lowest unoccupied molecular orbital (LUMO) of compounds 1 and 2 have been calculated on the optimized structure by using density functional theory (DFT). As shown in Fig. 3 and Table 1, the orbital distributions of HOMO and HOMO -1 for compounds 1 and 2 are localized on the carbazole units and the neighboring naphthalimide rings, and the energy difference between HOMO and HOMO - 1 is very small (0.03 eV for compound 1, 0 eV for compound 2). The electron densities of the LUMO are primarily located on the phosphorus(v) porphyrin cores. Therefore, the strong electron density relocation between HOMO (or HOMO - 1)

Fig. 3 The frontier orbital plots of the HOMO - 1, HOMO and LUMO for compounds 1 and 2.

and LUMO in the synthesized D-A-D type phosphorus(v) porphyrins makes it possible that photo-induced electron transfer might occur from the donors to the phosphorus(v) porphyrin rings.32

Electrochemical properties

To estimate the HOMO level of the phosphorus(v) porphyrins, cyclic voltammetry has been employed using a three-electrode cell and an electrochemistry workstation (CHI 604). A platinum button is used as the working electrode, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode under a N2 atmosphere. The cyclic voltammetry (CV) diagrams of compounds 1 and 2 in dichloromethane with Bu_4NBF_4 as the supporting electrolyte are shown in Fig. S4⁺, and the corresponding electrochemical data are listed in Table 1. The redox potential of Fc/Fc⁺, which possesses an absolute energy level of -4.8 eV relative to the vacuum level for calibration, is located at 0.66 eV at a scan rate of 100 mV s^{-1} . Therefore, the evaluation of the HOMO and LUMO energy levels could be estimated according to the following equations:

HOMO (eV) =
$$-(E_{ox} + 4.14)$$
 eV (1)

LUMO (eV) =
$$-(E_{red} + 4.14)$$
 eV (2)

where E_{ox} and E_{red} are the measured potentials relative to the standard calomel electrode (SCE). As a result, the HOMO energy levels are -5.35 eV and -5.13 eV for compounds 1 and 2, respectively. The higher HOMO energy level for compound 2 compared with that of compound 1 suggests that the electrondonating ability would be enhanced by increasing the length of the conjugation in axial functional carbazolylvinylnaphthalimide units.

Photovoltaic characterizations

To confirm the occurrence of the photo-induced electron transfer in D-A-D type phosphorus(v) porphyrins 1 and 2, devices with a configuration structure of [ITO/PEDOT : PSS/organic active film/ LiF/Al] have been fabricated. The photovoltaic data are obtained using a 150 W xenon light source that is focused to give 100 mW cm⁻², the equivalent of one sun at AM 1.5, at the surface of the test device. The IPCE values are determined with 2 nm intervals. The IPCE spectrum is recorded as a function of the excitation wavelength. As shown in Fig. 4, the IPCE response of the device based on compound 1 is quite low, and

Table 1 Electrochemical data and energy levels of phosphorus(v) porphyrins 1 and 2

Compound	Potential $(E_{1/2})$ V versus SCE				
	Oxidation ^a	Reduction ^b	$E_{\rm g}^{\ c}~({\rm eV})$	$HOMO^{d}$ (eV)	HOMO – $1/HOMO/LUMO^{e}$ (eV)
1 2	1.21 0.99	0.59 0.59	1.95 1.96	-5.35 -5.13	-6.32/-6.29/-4.64 -5.61/-5.61/-4.72

^a Ground state oxidation potential (first oxidation peak) of the compounds were measured in CH_2Cl_2 with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference. ^b Ground state reduction potential (first reduction peak). $^{c}E_{g}$ was determined from the edge of the absorption spectrum. ^d HOMO $(eV) = -(E_{ox} + 4.14) eV$. ^e The energy levels of HOMO - 1, HOMO and LUMO versus vacuum were given after geometrical optimization.







Fig. 4 IPCE spectra of the devices based on the phosphorus(v) porphyrins 1 and 2.

the highest IPCE value is 0.20% at the Soret band. However, the device based on compound 2 gives an obvious photovoltaic response, the IPCE spectrum is similar to the absorption one, and the highest IPCE value reaches 2.76% at the Soret band. The reason that the device based on compound 2 shows a more efficient photovoltaic response to visible light than 1 might be due to the lower oxidation potential of the more extended conjugated axial carbazolylvinylnaphthalimide units, which might lower the energy level of the charge separated state.³³ In addition, the stronger light-harvesting ability of compound 2 than 1 might be helpful for the enhanced IPCE response. Notably, the IPCE response of the devices suggests that the electron transfer from the axial carbazolylvinylnaphthalimide units to the phosphorus(v) porphyrin cores in compounds 1 and 2 indeed happens under illumination.³⁴ Therefore, the phosphorus(v) porphyrins might be good candidates for photovoltaic materials that could be applied in solar cells due to their broad absorption in the visible region.³⁵

Conclusions

In summary, the phosphorus(v) porphyrins 1 and 2 bearing axial carbazolylvinylnaphthalimide moieties have been synthesized. It is found that a photo-induced electron transfer occurs from the donors of the carbazolylvinylnaphthalimide to the acceptor of the phosphorus(v) porphyrin core. The IPCE maximum of 2.76% is achieved for the device based on compound 2, which is much higher than that of 1 due to the lower oxidation potential and the strong light-harvesting ability of the extended conjugation of the axial units. Therefore, phosphorus(v) porphyrins functionalized with axial conjugated units might become good candidates for photovoltaic materials that could be applied in solar cells.

Experimental section

Materials and measurements

¹H NMR spectra were recorded on a Mercury plus 500 MHz and 600 MHz, and Varian 300 MHz using CDCl₃ or DMSO-d₆ as the solvents. ¹³C NMR spectra were recorded on a Mercury plus 125 MHz and Varian 75 MHz at 298 K using CDCl₃ as the

solvent and tetramethylsilane (TMS) as the standard. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC spectrophotometer. Photoluminescence (PL) spectra were carried out on a Shimadzu RF-5301 luminescence spectrometer. FT-IR spectra were measured using a Germany Bruker vertex 80v FT-IR spectrometer by incorporating samples in KBr disks. Mass spectra were performed on Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) MS (COMPACT). HRMS spectra were determined on a 1290-microTOF Q II spectrograph (Agilent). C, H and N analyses were taken on a Perkin-Elmer 240C elemental analyzer. Cyclic voltammetry (CV) was performed using a CHI 604B electrochemical working station in CH₂Cl₂ containing 0.1 M Bu₄NBF₄ as a supporting electrolyte at room temperature. A platinum button was used as a working electron and a platinum wire as a counter electrode. The potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was maintained at 100 mV s^{-1} . The IPCE spectral output of the lamp was matched with the aid of a Mega-9 AM 1.5 sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum. A similar data acquisition system was used to control the IPCE measurement. Under full computer control, light from a 250 W halogen lamp was focused through a high throughput monochromator (Omni-150) onto the photovoltaic device under test. THF was refluxed with sodium and benzophenone. DMF was distilled from phosphorous pentoxide. Pyridine and dichloromethane were dried by CaH₂, and other chemicals were used as received without further purification.

Synthetic procedures and characterizations

4-Bromo-*N*-(4'-methoxyphenyl)-1,8-naphthalimide, dichloride 5,10,15,20-tetraphenyl phosphorus(v) porphyrin and compound **12** were synthesized according to the reported procedures.^{22,36,37}

9-Octyl-9H-carbazole-3-carbaldehyde (3). Phosphoryl chloride (6.12 g, 40 mmol) was added slowly to dry DMF (5 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. Then, a solution of 9-octyl-9H-carbazole (5.6 g, 20 mmol) in 1,2-dichloroethane (30 mL) was added. After stirring at room temperature for another 1 h, the mixture was refluxed for 10 h. Finally, the solution was cooled to room temperature and poured into 300 mL water. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), the organic phase was collected and washed with brine, and then dried with anhydrous MgSO₄. After the solvent was removed, the crude product was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate (v/v = 6/1) as eluent, followed by recrystallization in petroleum ether (60-90 °C) to give a pale yellow solid in a yield of 75%. Mp: 60.0–62.0 °C. ¹H NMR (300 MHz, TMS, CDCl₃): $\delta = 10.07$ (s, 1H), 8.58 (s, 1H), 8.13 (d, J = 7.5 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 7.54–7.49 (m, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.33–7.28 (m, 1H), 4.31–4.27 (m, 2H), 1.91–1.81 (m, 2H), 1.33–1.23 (m, 10H), 0.85 (t, J = 6.6 Hz, 3H) (see Fig. S5⁺); IR (KBr, cm⁻¹): 2920, 2360, 2030, 1600, 1380, 1140, 1070, 995, 864, 619, 515; Elemental analysis calculated for C₂₁H₂₅NO: C 82.04, H 8.20, N 4.56. Found C 81.86, H 8.26, N 4.65; MS, m/z: cal: 307.4, found 308.5 (Fig. S6⁺).

6-Iodo-9-octyl-9H-carbazole-3-carbaldehyde (4). Compound 3 (3.07 g, 10 mmol) was dissolved in 50 mL glacial acetic acid, and then KI (1.1 g, 6.7 mmol) and KIO₃ (0.86 g, 4 mmol) were added. The mixture was stirred at 80 °C until I2 was fully consumed. After that, the mixture was cooled to room temperature, and a yellow solid appeared. The solid was collected by filtration, and then poured into 5% NaHSO₃ (300 mL) to clear KIO₃. The resulting precipitate was filtered off, followed by recrystallization in ethanol to afford white solid in a yield of 76%. Mp: 106.0–108.0 °C. ¹H NMR (300 MHz, TMS, CDCl₃): $\delta = 10.08$ (s, 1H), 8.52 (d, J = 1.2 Hz, 1H), 8.44 (d, J = 1.5 Hz, 1H), 8.02 (m, 1H), 7.76 (m, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 4.28 (t, J = 7.2 Hz, 2H), 1.90–1.80 (m, 2H), 1.34–1.22 (m, 10H), 0.85 (t, J = 3.6 Hz, 3H); IR (KBr, cm⁻¹): 2920, 1690, 1620, 1590, 1280, 1130, 885, 808, 775; Elemental analysis calculated for C₂₁H₂₄INO: C 58.21, H 5.58, N 3.23. Found C 57.96, H 5.44, N 3.35; MS, m/z: cal: 433.3, found 434.0.

9-Octyl-3-vinyl-9H-carbazole (5). Potassium tert-butoxide (1.75 g, 15.6 mmol) was added to a solution of triphenylmethylphosphonium iodine (7.9 g, 19.5 mmol) in anhydrous THF (40 mL). After the mixture was stirred for 20 min at room temperature, 9-octyl-9H-carbazole-3-carbaldehyde 3 (4.00 g, 13.0 mmol) was added at 0 °C. Then, the mixture was stirred at room temperature for another 2 h, followed by pouring into 300 mL water. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the organic phase was collected and washed with brine. Then, it was dried with anhydrous MgSO₄. After the solvent was removed, the residue was purified by column chromatography (silica gel) with petroleum ether (60-90 °C) as eluent to afford 3.58 g (90%) of compound 5 as colorless oil. ¹H NMR (300 MHz, TMS, CDCl₃): $\delta = 8.16$ (t, J = 7.5 Hz, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.52–7.42 (m, 2H), 7.29 (d, J = 2.7 Hz, 1H), 7.03–6.93 (m, 1H), 5.85 (d, J = 17.4 Hz, 1H), 5.27 (d, J = 11.1 Hz, 1H), 4.30 (t, J = 7.2 Hz, 2H), 1.92-1.88 (m, 2H), 1.38-1.25 (m, 10H), 0.94 (t, J =4.8 Hz, 3H) (see Fig. S7[†]); IR (KBr, cm⁻¹): 3050, 2930, 2850, 1600, 1490, 1350, 1230, 1150, 987, 887, 806, 748, 735, 546; Elemental analysis calculated for C₂₂H₂₇N: C 86.51, H 8.91, N 4.59. Found C 86.40, H 8.78, N 4.80; MS, m/z: cal: 305.5, found 305.2 (Fig. S8[†]).

9-Octyl-6-((E)-2-(9-octyl-9H-carbazol-6-yl)vinyl)-9H-carbazole-3-carbaldehyde (6). A mixture of 6-iodo-9-octyl-9H-carbazole-3-carbaldehyde 4 (2.0 g, 4.62 mmol), 9-octyl-3-vinyl-9H-carbazole 5 (1.55 g, 5.08 mmol), anhydrous potassium carbonate (1.28 g, 9.24 mmol), tetrabutylammonium bromide (1.64 g, 5.08 mmol), and Pd(OAc)₂ (12 mg) in dry DMF (30 mL) under nitrogen atmosphere was stirred at 110 °C for 12 h. Then, the mixture was cooled to room temperature and poured into 300 mL water with stirring. After extraction with CH_2Cl_2 (3 × 50 mL), the organic phase was washed with brine and dried with anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography (silica gel) with petroleum ether/CH₂Cl₂ (v/v = 2/3) as eluent, followed by recrystallization in THF/EtOH to afford a yellow solid in a yield of 76%. Mp: 109.0–111.0 °C. ¹H NMR (500 MHz, TMS, CDCl₃): δ = 10.11 (s, 1H), 8.64 (d, J = 1.0 Hz, 1H), 8.31 (d, J = 1.0 Hz, 1H),

8.27 (d, J = 1.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.02–8.00 (m, 1H), 7.76 (m, 1H), 7.72 (m, 1H), 7.49–7.32 (m, 7H), 7.25 (s, 1H), 4.33–4.28 (m, 4H), 1.92–1.84 (m, 4H), 1.40–1.24 (m, 20H), 0.88–0.85 (m, 6H) (see Fig. S9†); IR (KBr, cm⁻¹): 3130, 2920, 2030, 1600, 1380, 1070, 995, 951, 862, 621, 515; Elemental analysis calculated for C₄₃H₅₀N₂O: C 84.55, H 8.25, N 4.59. Found C 84.37, H 8.17, N 4.43; MS, *m/z*: cal: 610.9, found 610.8 (Fig. S10†).

9-Octyl-3-((*E***)-2-(9-octyl-9***H***-carbazol-6-yl)vinyl)-6-vinyl-9***H***-carbazole (7). Compound 7 was prepared from compound 6 following the similar procedure for compound 5 in a yield of 78% as a white solid. Mp: 110.0–112.0 °C. ¹H NMR (500 MHz, TMS, CDCl₃): \delta = 8.27 (s, 2H), 8.16 (m, 2H), 7.72 (m, 2H), 7.58 (m, 1H), 7.47 (m, 1H), 7.40 (m, 3H), 7.36 (t, J = 5.5 Hz, 3H), 7.33 (s, 1H), 6.96–6.90 (m, 1H), 5.80 (d, J = 17.5 Hz, 1H), 5.22 (d, J = 11.5 Hz, 1H), 4.31–4.26 (m, 4H), 1.86 (m, 4H), 1.35–1.25 (m, 20H), 0.88–0.85 (m, 6H) (see Fig. S11); IR (KBr, cm⁻¹): 3130, 2360, 2020, 1600, 1380, 1070, 951, 860, 619, 515; Elemental analysis calculated for C₄₄H₅₂N₂: C 86.79, H 8.61, N 4.60. Found C 86.53, H 8.52, N 4.63; MS,** *m/z***: cal: 608.9, found 608.5 (Fig. S12†).**

4-[(E)-2-(9-Octyl-9H-carbazol-3-yl)vinyl]-N-(4'-methoxyphenyl)-1,8-naphthalimide (8). A mixture of 9-octyl-3-vinyl-9H-carbazole 5 (1.45 g, 4.75 mmol), 4-bromo-N-(4'-methoxy phenyl)-1,8-naphthalimide (1.65 g, 4.32 mmol), anhydrous potassium carbonate (1.19 g, 8.64 mmol), tetrabutylammonium bromide (1.53 g, 4.75 mmol), and Pd(OAc)₂ (12 mg) in dry DMF (10 mL) was stirred under nitrogen atmosphere at 110 °C for 12 h. Then, the mixture was cooled to room temperature and poured into 300 mL water with stirring. The resulting precipitate was filtered off and washed with water. The crude product was purified by column chromatography (silica gel) with dichloromethane/petroleum ether (60–90 °C) (v/v = 3/1) as eluent, followed by recrystallization in a dichloromethane/petroleum ether (60-90 °C) mixture to afford an orange-yellow solid in a yield of 72%. Mp: 216.0–218.0 °C. ¹H NMR (300 MHz, TMS, CDCl₃): $\delta = 8.74 - 8.63$ (m, 3H), 8.37 (d, J = 1.2 Hz, 1H), 8.16 (d, J =7.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 15.9 Hz, 1H), 7.85–7.79 (m, 2H), 7.60 (d, J = 15.9 Hz, 1H), 7.54–7.43 (m, 3H), 7.29 (m, 2H), 7.24 (m, 1H), 7.09 (m, 1H), 7.06 (t, J =2.4 Hz, 1H), 4.33 (t, J = 7.2 Hz, 2H), 3.88 (d, J = 2.1 Hz, 3H), 1.96-1.86 (m, 2H), 1.46-1.26 (m, 10H), 0.89-0.82 (m, 3H) (see Fig. S13[†]); IR (KBr, cm⁻¹): 3130, 2920, 2030, 1600, 1380, 1170, 1070, 995, 953, 862, 619, 517; Elemental analysis calculated for C₄₁H₃₈N₂O₃; C 81.16, H 6.31, N 4.62. Found C 81.08, H 6.25, N 4.73; MS, *m/z*: cal: 606.8, found 607.6 (Fig. S14⁺).

4-[*(E)*-2-(9-Octyl-9*H*-6-(*(E)*-2-(9-octyl-9*H*-carbazol-3-yl)vinyl)carbazol-3-yl)vinyl]-*N*-(4'-methoxyphenyl)-1,8-naphthalimide (9). According to the synthetic procedure of compound **8**, compound 9 was prepared from compound **7** and 4-bromo-*N*-(4'-methoxy phenyl)-1,8-naphthalimide in a yield of 65% as a deep red solid. Mp: 228.0–230.0 °C. ¹H NMR (300 MHz, TMS, CDCl₃): δ = 8.75 (d, *J* = 8.4 Hz, 1H), 8.69 (d, *J* = 6.9 Hz, 1H), 8.65 (d, *J* = 3.9 Hz, 1H), 8.42 (s, 1H), 8.33 (s, 1H), 8.28 (d, *J* = 1.2 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 15.9 Hz, 1H), 7.86–7.71 (m, 4H), 7.61 (d, *J* = 15.9 Hz, 1H), 7.51–7.46 (m, 2H), 7.51–7.38 (m, 7H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.25–7.23 (m, 2H), 4.35–4.28 (m, 4H), 3.88 (s, 3H), 1.94–1.87 (m, 4H), 1.41–1.26 (m, 20H), 0.90–0.85 (m, 6H) (see Fig. S15†); IR (KBr, cm⁻¹): 3130, 2920, 2030, 1600, 1380, 1170, 1070, 995, 951, 860, 621, 517; Elemental analysis calculated for $C_{63}H_{63}N_3O_3$: C 83.13, H 6.98, N 4.62. Found C 82.89, H 6.76, N 4.74; MS, *m/z*: cal: 910.2, found 910.8 (Fig. S16†).

4-[(E)-2-(9-Octvl-9H-carbazol-3-vl)vinvl]-N-(4'-hvdroxyphenvl)-1,8-naphthalimide (10). A solution of BBr₃ in anhydrous CH₂Cl₂ (1 M, 4 mL) was added dropwise to a solution of compound 8 (1.5 g, 2.47 mmol) in dry CH₂Cl₂ (50 mL) at -78 °C under a nitrogen atmosphere. The resulting solution was stirred at -78 °C for 2 h, and was then gradually warmed to room temperature. After the mixture was stirring at room temperature for another 15 h, it was poured into 300 mL water with stirring to quench excess BBr₃. After extraction with CH_2Cl_2 (3 × 50 mL), the organic phase was washed with water and dried with anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography (silica gel) with dichloromethane/methanol (v/v = 40/1) to afford a red power in a yield of 92%. Mp: 222.0-224.0 °C. ¹H NMR (300 MHz, TMS, CDCl₃): $\delta = 8.72 - 8.62$ (m, 3H), 8.36 (s, 1H), 8.15 (d, J =7.5 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 15.9 Hz, 1H), 7.83–7.78 (m, 2H), 7.60 (d, J = 15.6 Hz, 1H), 7.54–7.48 (m, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.17–7.11 (m, 2H), 6.89–6.87 (m, 1H), 6.85–6.84 (m, 1H), 6.21 (s, 1H), 4.31 (t, J = 7.5 Hz, 2H), 1.94–1.85 (m, 2H), 1.40–1.26 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H) (see Fig. S17[†]); IR (KBr, cm⁻¹): 3380, 3130, 2360, 2020, 1600, 1380, 1070, 995, 953, 862, 620, 515; Elemental analysis calculated for C₄₀H₃₆N₂O₃: C 81.05, H 6.21, N 4.73. Found C 80.87, H 6.12, N 4.65; MS, *m/z*: cal: 592.7, found 593.3 (Fig. S18[†]).

4-[(E)-2-(9-Octyl-9H-6-((E)-2-(9-octyl-9H-carbazol-3-yl)vinyl)carbazol-3-yl)vinyl]-N-(4'-hydroxyphenyl)-1,8-naphthalimide (11). By following the synthetic procedure for compound 10, compound 11 was prepared from compound 9 (2.2 g, 2.4 mmol), and the crude product was purified by column chromatography (silica gel) with $CH_2Cl_2/MeOH$ (v/v = 35/1) as eluent to afford a red powder in a yield of 65%. Mp: 224.0-226.0 °C. ¹H NMR (300 MHz, TMS, DMSO-d₆): δ = 9.65 (s, 1H), 8.70 (d, J = 9.6 Hz, 1H), 8.39-8.31 (m, 2H), 8.22 (d, J = 6.9 Hz, 1H), 8.19 (s, 1H), 8.07 (s, 1H), 7.93–7.55 (m, 7H), 7.41–7.25 (m, 6H), 7.06 (s, 4H), 6.86 (s, 4H), 4.09 (s, 4H), 1.71-1.48 (m, 4H), 1.10 (s, 20H), 0.75-0.67 (m, 6H) (see Fig. S19⁺); IR (KBr, cm⁻¹): 3380, 3130, 2920, 2020, 1600, 1380, 1170, 1070, 995, 953, 860, 619, 515; Elemental analysis calculated for $C_{62}H_{61}N_3O_3$:C 83.09, H 6.86, N 4.69. Found C 82.78, H 6.67, N 4.87; MS, *m*/*z*: cal: 896.2, found 896.5 (Fig. S20[†]).

Di[4-[(*E*)-2-(9-Octyl-9*H*-carbazol-3-yl)vinyl]-*N*-(4' hydroxyphenyl)-1,8-naphthalimide]5,10,15,20-tetraphenylporphyrinato phosphorus(v) chloride (1). Compound 10 (0.77 g, 1.3 mmol) and dichloride 5,10,15,20-tetraphenyl phosphorus(v) porphyrin (0.1 g, 0.13 mmol) were dissolved in dry pyridine (30 mL). The mixture was refluxed for 8 h under a nitrogen atmosphere. The solvent was evaporated, and the crude product was purified by column chromatography (silica gel) with dichloromethane/ methanol (v/v = 15/1) as eluent to afford a black solid in a yield of 71%. Mp: >250 °C. ¹H NMR (600 MHz, TMS, CDCl₃): δ = 9.16 (d, *J* = 3.0 Hz, 8H), 8.69 (d, *J* = 8.4 Hz, 2H), 8.50 (d, J = 7.2 Hz, 2H), 8.45 (d, J = 7.8 Hz, 2H), 8.33 (s, 2H), 8.14 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.91-7.88 (m, 10H), 7.82 (d, J = 3.6 Hz, 12H), 7.79–7.75 (m, 4H), 7.73–7.71 (m, 1H), 7.56 (d, J = 15.6 Hz, 2H), 7.53–7.51 (m, 1H), 7.50 (s, 1H), 7.49 (s, 1H), 7.44 (t, J = 7.2 Hz, 4H), 7.28 (d, J = 7.2 Hz, 4H), 5.97 (d, J = 7.8 Hz, 4H), 4.33–4.30 (m, 4H), 1.92-1.88 (m, 4H), 1.34-1.24 (m, 20H), 0.86 (t, J = 6.9 Hz, 6H) (see Fig. S21[†]); ¹³C NMR (75 MHz, CDCl₃): δ = 163.9, 163.7, 149.0, 148.8, 142.8, 141.0, 140.9, 139.4, 137.0, 134.6, 134.1, 133.5, 133.4, 131.4, 130.8, 130.7, 130.0, 129.6, 129.5, 128.9, 128.7, 128.4, 127.5, 126.5, 126.1, 125.0, 123.3, 123.2, 122.7, 122.6, 120.4, 120.1, 120.0, 119.7, 119.3, 117.5, 115.1, 115.0, 109.2, 109.0, 43.2, 31.7, 29.3, 29.0, 28.9, 27.2, 22.5, 14.0 (see Fig. S22[†]); IR (KBr, cm⁻¹): 3140, 2910, 2440, 2030, 1600, 1380, 1170, 1070, 951, 860, 546, 515; Elemental analysis calculated for C124H98ClN8O6P: C 79.96, H 5.30, N 6.02. Found C 79.78, H 5.26, N 6.12; MS, m/z: cal: 1827.1 [M⁺ - Cl], found 1827.6 [M⁺ - Cl] (Fig. S23[†]); HRMS cal: 1827.1287 $[M^+ - Cl]$, found: 1826.7260 $[M^+ - Cl]$ (Fig. S24[†]).

Di[4-[(E)-2-(9-Octyl-9H-6-((E)-2-(9-octyl-9H-carbazol-3-yl)vinyl)carbazol-3-vl)vinvl]-N-(4'-hvdroxyphenvl)-1,8-naphthalimide]-5,10,15,20-tetraphenylporphyrinato phosphorus(v) chloride (2). Compound 2 was prepared from compounds 11 (1.2 g, 1.33 mmol) and dichloride 5,10,15,20-tetraphenyl phosphorus(v) porphyrin (0.1 g, 0.13 mmol) under similar reaction conditions for the synthesis of compound 1 except the reaction time was prolonged to 12 h, and the crude product was purified by column chromatography (silica gel) with dichloromethane/ methanol (v/v = 12/1) as eluent to afford a black solid in a yield of 60%. Mp: >250 °C. ¹H NMR (600 MHz, TMS, CDCl₃): δ = 9.16 (s, 8H), 8.70 (d, J = 8.4 Hz, 2H), 8.50 (d, J = 7.2 Hz, 2H), 8.46 (d, *J* = 7.2 Hz, 2H), 8.37 (s, 2H), 8.30 (s, 2H), 8.25 (s, 2H), 8.12 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 7.2 Hz, 2H), 7.90 (s, 10H), 7.82 (s, 14H), 7.76 (t, J = 10.2 Hz, 4H), 7.72 (t, J = 10.2 Hz, 4H), 7.56 (d, J = 15.6 Hz, 2H), 7.47 (t, J = 7.2 Hz, 3H), 7.43–7.40 (m, 9H), 7.36 (d, J = 6.0 Hz, 4H), 7.23 (d, J = 7.2 Hz, 2H), 5.98 (d, J = 8.4 Hz, 4H), 4.30 (m, 8H), 1.93–1.86 (m, 8H), 1.33-1.25 (m, 40H), 0.86 (t, J = 7.2 Hz, 12H) (see Fig. S25⁺); ¹³C NMR (125 MHz, CDCl₃): δ = 164.0, 163.8, 149.1, 148.9, 142.8, 141.4, 140.9, 140.4, 140.1, 139.5, 137.1, 134.7, 134.2, 133.6, 131.5, 131.4, 130.8, 130.1, 129.7, 129.6, 129.0, 128.8, 128.5, 127.7, 127.6, 126.7, 125.3, 124.9, 124.2, 123.5, 123.3, 123.2, 122.9, 120.4, 120.2, 120.1, 119.7, 118.9, 118.9, 118.3, 118.2, 117.6, 115.2, 109.4, 108.9, 43.4, 43.2, 31.8, 29.7, 29.4, 29.2, 29.0, 27.3, 22.6, 14.1 (see Fig. S26⁺); IR (KBr, cm⁻¹): 3140, 2920, 2440, 2020, 1600, 1380, 1170, 1070, 951, 860, 546, 515; Elemental analysis calculated for $C_{68}H_{148}CIN_{10}O_6P$: C 81.71, H 6.04, N 5.67. Found C 81.59, H 5.86, N 5.69; MS, m/z: cal: 2434.0 [M⁺ – Cl], found 2434.5 [M⁺ – Cl] (Fig. S27⁺); HRMS cal: 2434.0099 $[M^+ - Cl]$, found: 2434.0588 $[M^+ - Cl]$ (Fig. S28[†]).

Theoretical calculation methods

The geometrical structures of compounds 1 and 2 were optimized by employing the density functional theory at the B3LYP/ 6-31 level with the Gaussian 03W program package. Molecular orbitals were visualized using Gaussview.

Preparation of photovoltaic devices

The device was fabricated on glass substrates pre-coated with indium tin oxide (ITO) modified by a PEDOT: PSS (Clevios P VP Al 4083) layer. The ITO-coated glass substrates were ultrasonicated for 20 min in toluene, acetone and Hellmanex soap water (2%), followed by extensive rinsing and ultrasonication in deionized water and isopropyl alcohol. The substrates were then dried under IR radiation. After that, the ITO glass substrates were spin-coated (3000 rpm, 60 s) with a PEDOT: PSS layer of thickness about 20 nm and dried for 1 h at 90 °C in air on a hot plate. The solutions for the active layer were prepared by dissolving compounds 1 and 2 (10 mg) in chloroform (1 mL). The solution was then spin-cast at 1000 rpm on top of the PEDOT : PSS layer. The optimized thicknesses of the active layers are 75 nm for compound 1 and 60 nm for compound 2. Then, LiF (3 nm) and Al (100 nm) layers were subsequently deposited on the active layer under vacuum (5 \times 10⁻⁴ Pa). The devices were removed into a nitrogen glove-box and annealed by placing on hot plates for 20 min at 70 °C. After annealing, the samples were cooled to room temperature. Finally, the device of [ITO/PEDOT : PSS/organic active film/LiF/Al] was fabricated.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (20874034 and 51073068), 973 Program (2009CB939701), NSFC-JSPS Scientific Cooperation Program (21011140069) and Open Project of State Key Laboratory of Supramolecular Structure and Materials (SKLSSM201203).

Notes and references

- (a) M. E. El-Khouly, S. H. Shim, Y. Araki, O. Ito and K. Y. Kay, *J. Phys. Chem. B*, 2008, **112**, 3910–3917; (b) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198–205; (c) G. Bottari, G. D. Torre, D. M. Guidi and T. Torres, *Chem. Rev.*, 2010, **110**, 6768–6816.
- (a) A. Harriman and J. P. Sauvage, Chem. Soc. Rev., 1996, 25, 41–48;
 (b) M. S. Choi, T. Yamazaki and T. Aida, Angew. Chem., Int. Ed., 2004, 43, 150–158;
 (c) N. Aratani, H. S. Cho, T. K. Ahn, S. Cho, D. Kim, H. Sumi and A. Osuka, J. Am. Chem. Soc., 2003, 125, 9668–9681.
- 3 (a) H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda and A. Osuka, J. Am. Chem. Soc., 2002, **124**, 14642–14654; (b) Y. Tanaka, H. Mori, T. Koide, H. Yorimitsu, N. Aratani and A. Osuka, Angew. Chem., Int. Ed., 2011, **50**, 11460–11464; (c) M. Ishida, J.-Y. Shin, J. M. Lim, B. S. Lee, M.-C. Yoon, T. Koide, J. L. Sessler, A. Osuka and D. H. Kim, J. Am. Chem. Soc., 2011, **133**, 15533–15544.
- 4 D. Gust and T. A. Moore, Science, 1989, 244, 35-41.
- 5 M. R. Wasielewski, Chem. Rev., 1992, 92, 435-461.
- 6 K. Hirakawa and H. Segawa, J. Photochem. Photobiol., A, 1999, 123, 67–76.
- 7 (a) F. Zeng and S. C. Zimmerman, Chem. Rev., 1999, 99, 1747–1786;
 (b) P. Ceroni, G. Bergamini, F. Marchioni and V. Balzani, Prog. Polym. Sci., 2005, 30, 453–473;
 (c) D. L. Jiang and T. Aida, Nature, 1997, 388, 454–456;
 (d) K. R. J. Thomas, A. L. Thompson, A. V. Sivakumar, C. J. Bardeen and S. Thayumanavan, J. Am. Chem. Soc., 2005, 127, 373–383;
 (e) A. Nantalaksakul, R. R. Dasari, T. S. Ahn, R. A. Kaysi, C. J. Bardeen and S. Thayumanavan, Org. Lett., 2006, 8, 2981–2984.
- F. Wurthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port and H. C. Wolf, *J. Am. Chem. Soc.*, 1995, **117**, 8090–8099; (b) G. J. Capitosti, S. J. Cramer, C. S. Rajesh and D. A. Modarelli, *Org. Lett.*, 2001, **3**, 1645–1648; (c) K. Onitsuka, H. Kitajima, M. Fujimoto, A. Luchi, F. Takei and S. Takahashi, *Chem. Commun.*, 2002, 2576–2577;

(d) W. R. Dichtel, S. Hecht and J. M. J. Fréchet, Org. Lett., 2005, 7, 4451-4454.

- 9 (a) X. L. Liu, R. Lu, T. H. Xu, D. F. Xu, Y. Zhan, P. Chen, X. P. Qiu and Y. Y. Zhao, *Eur. J. Org. Chem.*, 2009, 53–60; (b) T. H. Xu, R. Lu, X. P. Qiu, X. L. Liu, P. C. Xue, C. H. Tan, C. Y. Bao and Y. Y. Zhao, *Eur. J. Org. Chem.*, 2006, 4014–4020; (c) T. H. Xu, R. Lu, X. L. Liu, P. Chen, X. P. Qiu and Y. Y. Zhao, *J. Org. Chem.*, 2008, **73**, 1809–1817; (d) T. H. Xu, R. Lu, X. L. Liu, P. Chen, X. P. Qiu and Y. Y. Zhao, *Eur. J. Org. Chem.*, 2008, 1065–1071.
- 10 M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos and E. M. N. Mhuircheartaigh, *Adv. Mater.*, 2007, **19**, 2737– 2774.
- (a) F. Loiseau, S. Campagna, A. Hameurlaine and W. Dehaen, J. Am. Chem. Soc., 2005, 127, 11352–11363; (b) J. P. Collin, A. Harriman, V. Heitz, F. Odobel and J. P. Sauvage, J. Am. Chem. Soc., 1994, 116, 5679–5690; (c) A. K. Burrell, D. L. Officer and D. C. W. Reid, Chem. Rev., 2001, 101, 2751–2796.
- 12 (a) J. Seth, V. Palaniappan, R. W. Wagner, T. E. Johnson, J. S. Lindsey and D. F. Bocian, J. Am. Chem. Soc., 1996, **118**, 11194–11207; (b) A. Nakano, T. Yamazaki, Y. Nishimura, I. Yamazaki and A. Osuka, Chem.-Eur. J., 2000, **6**, 3254–3271.
- (a) K. Albrecht, Y. Kasai, A. Kimoto and K. Yamamoto, *Macromolecules*, 2008, 41, 3793–3800; (b) C. Zhang, Q. Wang, H. Long and W. Zhang, J. Am. Chem. Soc., 2011, 133, 20995–21001; (c) C. Huo, H. D. Zhang, H. Y. Zhang, H. Y. Zhang, B. Yang, P. Zhang and Y. Wang, *Inorg. Chem.*, 2006, 45, 4735–4732; (d) A. G. Hyslop, M. A. Kellett, P. M. Iovine and M. J. Therien, J. Am. Chem. Soc., 1998, 120, 12676–12677; (e) W. Maes, J. Vanderhaeghen, S. Smeets, C. V. Asokan, L. M. V. Renterghem, F. E. D. Prez, M. Smet and W. Dehaen, J. Org. Chem., 2006, 71, 2987–2994.
- 14 T. Barbour, W. J. Belcher, P. J. Brothers, C. E. F. Richard and D. C. Wave, *Inorg. Chem.*, 1992, **31**, 746–754.
- (a) Y. Z. Liu, H. Lin, J. T. Dy, K. Tamaki, J. Nakazaki, D. Nakayama, S. Uchida, T. Kubo and H. Segawa, *Chem. Commun.*, 2011, **47**, 4010– 4012; (b) K. Hirakawa, K. Saito and H. Segawa, *J. Phys. Chem. A*, 2009, **113**, 8852–8856; (c) K. Hirakawa and H. Segawa, *J. Photochem. Photobiol.*, *A*, 2010, **213**, 73–79.
- 16 (a) T. A. Rao and B. G. Maiya, *Inorg. Chem.*, 1996, 35, 4829–4836;
 (b) D. R. Reddy and B. G. Maiya, *J. Phys. Chem. A*, 2003, 107, 6326–6333;
 (c) A. Harriman, M. Mehrabi and B. G. Maiya, *Photochem. Photobiol. Sci.*, 2005, 4, 47–53;
 (d) P. P. Kumar, G. Premaladha and B. G. Maiya, *Chem. Commun.*, 2005, 3823–3825;
 (e) L. Giribabu, A. A. Kumar, V. Neeraja and B. G. Maiya, *Angew. Chem., Int. Ed.*, 2001, 40, 3621–3624.
- 17 T. H. Xu, R. Lu, X. L. Liu, X. Q. Zheng, X. P. Qiu and Y. Y. Zhao, Org. Lett., 2007, 5, 797–800.
- (a) J. F. Morin and M. Leclerc, *Macromolecules*, 2001, 34, 4680–4682;
 (b) J. F. Morin and M. Leclerc, *Macromolecules*, 2002, 35, 8413–8417;
 (c) N. Drolet, J. F. Morin, N. Leclerc, S. Wakim, Y. Tao and M. Leclerc, *Adv. Funct. Mater.*, 2005, 15, 1671–1682;
 (d) N. Drolet, J. F. Morin, N. Leclerc, *Adv. Funct. Mater.*, 2005, 15, 1671–1682.
- 19 (a) M. G. Ren, H. J. Guo, F. Qi and Q. H. Song, Org. Biomol. Chem., 2011, 9, 6913–6916; (b) C. Y. Zhang, Y. K. Che, X. M. Yang, B. R. Bunes and L. Zang, Chem. Commun., 2010, 46, 5560–5562.
- 20 (a) A. Vilsmeier and A. Haack, *Chem. Ber.*, 1927, **60**, 119; (b) H. Y. Wang, G. Chen, X. P. Xu, H. Chen and S. J. Ji, *Dyes Pigm.*, 2010, **86**, 238–248; (c) M. Todd, W. J. Li and L. P. Yu, *J. Am. Chem. Soc.*, 1997, **119**, 844–845.
- 21 H. F. Heck and J. P. Nolley, J. Org. Chem., 1972, 37, 2320-2322.
- 22 H. S. Cao, V. Chang, R. Hernandez and M. D. Heagy, J. Org. Chem., 2005, 70, 4929–4934.
- 23 (a) H. P. Zhou, R. Lu, X. Zhao, X. P. Qiu, P. C. Xue, X. L. Liu and X. F. Zhang, *Tetrahedron Lett.*, 2010, **51**, 5287–5290; (b) H. P. Zhou, X. Zhao, T. H. Huang, R. Lu, H. Z. Zhang, X. H. Qi, P. C. Xue, X. L. Liu and X. F. Zhang, *Org. Biomol. Chem.*, 2011, **9**, 1600– 1607.
- 24 (a) C. Hohle, U. Hofmann, S. Schloter, M. Thelakkat, P. Strohriegl, D. Haarer and S. J. Zilker, J. Mater. Chem., 1999, 9, 2205–2210;
 (b) T. Barbour, W. J. Belcher, P. J. Brothers, C. E. F. Rickard and D. C. Ware, Inorg. Chem., 1992, 31, 746–754; (c) K. Susumu, K. Kunimoto, H. Segawa and T. Shimidzu, J. Photochem. Photobiol., A, 1995, 92, 39–46; (d) K. Susumu, K. Kunimoto, H. Segawa and T. Shimidzu, J. Phys. Chem., 1995, 99, 29–34; (e) A. T. Rao and B. G. Maiya, Inorg. Chem., 1996, 35, 4829–4836.

- 25 Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamagushi and K. Tamao, *Angew. Chem., Int. Ed.*, 2003, 42, 2036–2040.
- 26 K. Nagao, Y. Takeuchi and H. Segawa, J. Phys. Chem. B, 2006, 110, 5120–5126.
- 27 N. Blouin and M. Leclerc, Acc. Chem. Res., 2008, 41, 1110-1119.
- 28 R. Grisorio, P. Mastrorilli, C. F. Nobile, G. Romanazzi, G. P. Suranna, G. Gigli, C. Piliego, G. Ciccarella, P. Cosma, D. Acierno and E. Amendola, *Macromolecules*, 2007, **40**, 4865–4873.
- (a) D. R. Reddy and B. G. Maiya, *Chem. Commun.*, 2001, 117–118;
 (b) M. Borgström, E. Blart, G. Boschloo, E. Mukhtar, A. Hagfeldt, L. Hammarström and F. Odobel, *J. Phys. Chem. B*, 2005, **109**, 22928–22934;
 (c) J. S. Yang, K. L. Liau, C. M. Wang and C. Y. Hwang, *J. Am. Chem. Soc.*, 2004, **126**, 12325–12335.
- 30 M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder and N. B. Mckeown, *Angew. Chem.*, *Int. Ed.*, 1998, 37, 1092–1094.

- 31 M. Borgstrom, E. Blart, G. Boschloo, E. Mukhtar, A. Hagfeldt, L. Hammarstrom and F. Odobel, J. Phys. Chem. B, 2005, 109, 22928–22934.
- 32 T. Honda, T. Nakanishi, K. Ohkubo, T. Kojima and S. Fukuzumi, *J. Phys. Chem. C*, 2010, **114**, 14290–14299.
- 33 M. Narutaki, K. Takimiya, T. Otsubo, Y. Harima, H. Zhang, Y. Araki and O. Ito, J. Org. Chem., 2006, 71, 1761–1768.
- 34 M. Borgström, E. Blart, G. Boschloo, E. Mukhtar, A. Hagfeldt, L. Hammarström and F. Odobel, J. Phys. Chem. B, 2005, 109, 22928–22934.
- 35 (a) A. Gouloumis, A. Escosura, P. Vázquez, T. Torres, A. Kahnt, D. M. Guldi, H. Neugebauer, C. Winder, M. Dress and N. S. Sariciftci, Org. Lett., 2006, 8, 5187–5190; (b) T. Hasobe, Y. Kashiwagi, M. A. Absalom, J. Sly, K. Hosomizu, M. J. Crossley, H. Imahori, P. V. Kamat and S. Fukuzumi, Adv. Mater., 2004, 16, 975–979.
- 36 A. D. Adler, F. G. Longo, J. D. Finarelli, J. Goldmacher and L. J. Koreakoff, J. Org. Chem., 1967, 32, 467–476.
- 37 F. A. Neugebauer and H. Fisher, Chem. Ber., 1972, 105, 2686-2693.