Mixed (porphyrinato)(phthalocyaninato) rare-earth(III) double-decker complexes for broadband light harvesting organic solar cells[†]

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Solution-processed organic-inorganic hybrid bulk heterojunction solar cells with the capability of broadband solar photon harvesting over the ultraviolet-visible-near-infrared spectral range are developed. A series of mixed (porphyrinato)(phthalocyaninato) rare-earth double-decker complexes, $[M^{III}H(TClPP){Pc(\alpha - OC_4H_9)_8}]$ (1–7; M = Y, Sm, Eu, Tb, Dy, Ho, Lu; TClPP = meso-tetrakis(4chlorophenyl)porphyrinate; $Pc(\alpha - OC_4H_9)_8 = 1,4,8,11,15,18,22,25$ -octakis(1-butyloxy) phthalocyaninate) and $[Y^{III}(TCIPP)(Pc)]$ (8, Pc = unsubstituted phthalocyaninate), along with a heteroleptic bis(phthalocyaninato) yttrium double-decker complex $[Y^{III}H(Pc){Pc(\alpha-OC_4H_9)_8}]$ (9), are synthesized and utilized as broadband absorbers and electron donors (D), whereas N,N'-bis(1ethylhexyl)-3,4:9,10-perylenebis(dicarbox-imide) (PDI) or [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) is adopted as primary electron acceptor (A₁). For suppressing the fatal back charge transfer at D/A_1 interface, the D:A₁ blend is fabricated within an *in situ* formed cheap inorganic network of nanoporous TiO_{x} , which can act as a secondary electron acceptor (A₂). For characterization of these structures, steady state spectroscopy, fluorescence dynamics, atomic force microscopy, current-voltage characteristics, and photoelectrical properties of the active materials or devices are investigated. Solar cells utilizing PDI as the primary acceptor show higher values in open circuit voltage, fill factor, and power conversion efficiency over those cells using PCBM as the primary acceptor. With a cell area of 0.36 cm^2 , good efficiencies of up to 0.82% are achieved by the aforementioned double-decker complex: PDI:TiO_x blends under 1-sun air mass 1.5 global illumination. These results conclude that doubledecker bis(tetrapyrrole) complexes are promising photovoltaic materials with tunable absorption and photophysical properties.

Introduction

Organic solar cells (OSCs) have attracted considerable attention during the last two decades owing to their potential to produce flexible, low-cost, and light-weight devices.^{1,2} Great and continuous progress in OSCs has been achieved either by solution processed conjugated polymer-fullerene blends or by vacuum or organic vapor phase deposited small-molecule materials in recent years.¹⁻⁸ The state-of-the-art power conversion efficiency has

now been steadily increased to 8.13% and 8.3% for polymer solar cells and small-molecule solar cells, respectively.^{9,10} Bulk heterojunction (BHJ) OSCs consist of interpenetrating networks and a bicontinuous phase,³ which are usually built up by organic electron donors and acceptors. Breakthroughs have been realized in the past few years by directly mixing soluble conjugated polymers with electron acceptors including not only organic semiconductors such as C₆₀, C₆₀ and C₇₀ derivatives and modified carbon nanotubes,^{3,4,11} but also inorganic semiconductor nanostructures such as TiO₂, ZnO, and CdSe.¹²⁻¹⁴ The use of BHJ architectures, composed of a polymer-fullerene blend within a cheap inorganic acceptor network of TiO2 nanostructures, was considered as one of the most promising and effective approaches.^{15,16} This approach provides more efficient pathways for both electrons and holes to the respective electrodes, resulting in enhanced charge transportation and collection inside the active layer.¹⁶ This approach is attractive for the fabrication of small-molecule BHJ solar cells as well.¹⁷

As a unique class of small-molecule organic semiconductors, phthalocyanines can act as prosperous donor materials in OSCs

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due to their high absorption coefficient in ultraviolet, visible and particularly near infrared region (610~750 nm), high hole mobility, and high photo- and thermo-stability.² Unsubstituted phthalocyanines are typically poorly soluble in organic solvents, necessitating costly vacuum or vapor phase deposition techniques for their assembly into solar cells.5-8 Solar cells utilizing CuPc as donor and C_{60} as acceptor have been most intensively investigated, reaching efficiencies as high as 5.0%.⁷ Various other unsubstituted phthalocyanines, such as H₂Pc, ZnPc, SnPc, AlClPc, PbPc, TiOPc, PdPc, and PtPc, have been deeply studied with successful photovoltaic applications as well.^{2,8} C₆₀ and 3,4,9,10-pervlene tetracarboxylic bisbenzimidazole (PTCBI) are among the most commonly used electron acceptors in these vacuum deposited phthalocyanine-based solar cells.² OSCs based on soluble substituted phthalocyanines by low-cost solution processing technique have become of great interest since very recently.¹⁸ In 2006 Torres and co-workers reported solution processed OSC of bis(C₆₀)-ZnPc triad with an efficiency of 0.024%.19 In 2009 Torres and co-workers reported solution processed BHJ cells made from a supramolecular squarainephthalocyanine ensemble (RuPc-Sq-RuPc) and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) having efficiencies of up to 0.285%.²⁰ In 2009 Bäuerle and Torres and co-workers reported solution processed BHJ solar cells made from RuPc complexes, which possess one or two axial dendritic oligothiophene ligands, and PCBM or PC71BM showing efficiencies of up to 1.6%.²¹ In 2010 Varotto et al. reported solution processed BHJ solar cells made from self-organized ZnPc derivatives blended with Py-C₆₀ showing an efficiency of 0.12%.22 In 2010 Liang et al. reported solution processed BHJ OSCs made from ZnPc-TDA, peripherally functionalized with donor-acceptor conjugates, and PCBM showing efficiencies of up to 0.4%.23 In 2011 Yan and coworkers reported solution processed organic-inorganic hybrid p-i-n heterojunction solar cells made from hyperbranched phthalocyanines sandwiched in between TiO_2 (or TiO_x) and CuSCN, with efficiencies of over 0.23%.24 From these results, it seems that there is a large room for cell efficiency improvement with solution-processed phthalocyanine-based solar cells.

Sandwich-type bis- and tris-(tetrapyrrole) complexes with large central metal ions including rare earth, actinide, early transition, and main group metals, have been fascinating chemists for several decades owing to their potential applications as versatile materials in various disciplines.²⁵ Considerable efforts have been devoted to the synthesis and investigations of electronic and optical properties of these complexes. Due to the intra- and inter-molecular $\pi - \pi$ interactions and the intrinsic nature of the metal centers, these complexes have shown extraordinary optical, electrical, thermodynamic and magnetic properties. They are expected to have great prospective applications in molecular electronic, photonic, and magnetic devices.²⁶ Moreover, their unique electronic and optical properties including broadband absorption (especially the wavelengths longer than 700 nm), large exciton delocalization length, and high carrier mobility make these complexes promising for photovoltaic applications.^{25,26} Sandwich-type bis(tetrapyrrole) complexes show a notable decrease of the first oxidation potentials (corresponding to highest occupied molecular orbital, HOMO) and increase of the first reduction potentials (corresponding to lowest unoccupied molecular orbital, LUMO)

compared to respective mono(tetrapyrrole) complexes.²⁵ As a result, they can serve as potent electron donors, electron acceptors, or ambipolar roles in charge-transfer materials.²⁷⁻²⁹ However, there are very few reports regarding successful photovoltaic cells made from bis- or tris-(tetrapyrrole) complexes. In 1998 Videlot et al. reported vacuum deposited OSCs of LnPc₂ (Ln = La, Nd, Eu, Gd, Lu) in Schottky and p-nheterojunction configurations.³⁰ In 2003 Liu et al. reported solution processed OSCs of $Ln(TBPc)_2$ (Ln = Tb, Dy) with N, N'-bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarbox-imide) (PDHEP).³¹ In 2004 Liu et al. reported solution processed BHJ solar cells made from Lu(TBPP)(TBPc) and PDHEP with or without TiO₂.³² Very low ($\sim 10^{-40}$) or no efficiencies were stated in these reports. Our previous work published in 2008 encouragingly demonstrated solution processed BHJ solar cells made from sandwiched (na)phthalocyaninato double- or triple-decker complexes (i.e. NcSm[Pc(OC₈H₁₇)₈] or PcSm[Pc(OC₈H₁₇)₈]Sm $[Pc(OC_8H_{17})_8]$) and N,N'-bis(1-ethylhexyl)-3,4:9,10-perylenebis (dicarbox-imide) (PDI) with or without nanostructured TiO₂ layers, showing efficiencies of over 0.36%.¹⁷

By virtue of all the aforementioned results we proposed to synthesize soluble mixed (porphyrinato)(phthalocyaninato) rareearth double-decker complexes for solution processed BHJ solar cells which can get extra benefit from the enhanced absorption in ultraviolet-visible-near-infrared range over those mono(tetrapyrrole) or homoleptic bis(tetrapyrrole) complexes. In this contribution, we describe in detail the photophysical properties and photovoltaic applications of a series of mixed (porphyrinato) (phthalocyaninato) rare-earth double-decker complexes [M^{III}H $(\text{TClPP})\{\text{Pc}(\alpha - \text{OC}_4\text{H}_9)_8\}$] (1–7; M = Y, Sm, Eu, Tb, Dy, Ho, TCIPP = meso-tetrakis(4-chlorophenyl)porphyrinate;Lu: $Pc(\alpha - OC_4H_9)_8 = 1,4,8,11,15,18,22,25$ -octakis(1-butyloxy)phthalocyaninate) and $[Y^{III}(TClPP)(Pc)]$ (8, Pc = unsubstituted phthalocyaninate), as well as a heteroleptic bis(phthalocyaninato) yttrium double-decker complex $[Y^{III}H(Pc)]$ Pc(α - $OC_4H_9_8$ [9) as shown in Fig. 1. To our knowledge, this is the first report for protonated mixed (porphyrinato)(phthalocyaninato) double-decker complexes in photovoltaic applications. Our preliminary results demonstrated the success in the development of new photovoltaic materials with broadband light harvesting capabilities.

Results and discussion

Steady-state absorption

Absorption spectra of sandwich-type porphyrinato and/or phthalocyaninato rare-earth complexes are dependent on the solvent employed.³³ In order to exclude the solvent effect, the absorption spectra of all the complexes **1–9**, PDI and PCBM as well as their mixtures were recorded in CH₂Cl₂. Fig. 2 shows the absorption spectra of **1–7**. As expected, the absorption spectra of **1–7** resemble those of other protonated mixed (porphyrinato) (phthalocyaninato) double-decker complexes including M^{III}H (TCIPP)[Pc(α -OC₅H₁₁)₄] [M = Y, Sm, Eu; Pc(α -OC₅H₁₁)₄ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate],³⁴ M^{III}H(TCIPP) [Pc(OBNP)₂] (M = Y, Eu; Pc(OBNP)₂ = binaphthyl-phthalocyaninate),³³ and Y^{III}H(TBPP)[Pc(α -OC₄H₉)₈].³⁵ These spectra show strong porphyrin and phthalocyanine Soret bands at



Fig. 1 Schematic molecular structures of the double-decker complexes 1–9, PDI, and PCBM.

418-421 nm and 324-325 nm, respectively, and several Q bands in the range of 571-950 nm. The spectra also display a medium band at 498-500 nm, which involves a delocalized orbital in the transition.^{36,37} A characteristic near-IR absorption at approximately 1200 nm for non-protonated complexes M^{III}(TClPP)[Pc $(\alpha$ -OC₅H₁₁)₄] [M = Y, Sm, Eu] was not observed for 1–7, which further confirmed the protonated nature of these complexes.³⁴ The positions of all the absorption bands are sensitive to the ionic radius of the metal centers with red or blue shift, depending on the nature of the different transitions. For instance, the absorption at 900-1050 nm gradually shifts to the red along with the lanthanide contraction, while a blue-shift was observed for the porphyrin Soret band at 418-421 nm. Owing to the close adjacency of the two conjugated π -systems arranged in a face-toface manner in 1–7, there are significant interactions between the two macrocyclic ligands. The changes of the positions of the absorption bands with respect to the metal centers are in accordance with the extent of π - π interaction, which increases as the size of the metal center decreases.

Fig. 3 shows the absorption spectra of 8, 9, PDI and PCBM in CH₂Cl₂. The absorption spectrum of the neutral mixed (por-phyrinato)(phthalocyaninato) yttrium complex 8 shows strong

bands at 331 and 401 nm, which can be attributed to the Soret bands of this complex having a predominant Pc and TCIPP character, respectively. The absorptions at 468 and 1027 nm are due to electronic transitions involving a semi-occupied orbital, which has a higher Pc character.^{38,39} The absorption at 1027 nm can be further attributed to the electronic transition from the semi-occupied orbital to a degenerated LUMO.38 An additional characteristic near-IR band for π -radical anions at 1238 nm (with a shoulder at 1656 nm) was observed in previous work when measured in CHCl₃, which is due to the transition from a second HOMO to the semi-occupied orbital.^{38,40} Furthermore, a weak absorption at 731 nm also appeared for this doubledecker. This band may be tentatively assigned to one of the Q band absorptions of this mixed double-decker complex. For the heteroleptic bis(phthalocyaninato) yttrium double-decker complex 9, its spectrum shows a typical B band at 330 nm, and multiple Q bands including one strong absorption at 697 nm, and several weak absorptions at 557 nm, 764 nm (shoulder), and 852 nm. The Q band splitting is due to the lowering of the molecular symmetry. In addition, one weak band at 496 nm was observed as well, which is probably related to a delocalized orbital.36,37



Fig. 2 Absorption spectra of $M^{III}H(TCIPP)\{Pc(\alpha - OC_4H_9)_8\}\}$ (M = Y, Sm, Eu, Tb, Dy, Ho, Lu; 1–7) in CH₂Cl₂. The spectra are stacked in the order of **2-3-4-5-1-6-7**, following the ionic radius contraction sequence of the rare-earth(III) cations within these complexes.

To facilitate comparison with other reported bis(tetrapyrrole) complexes, the absorption spectra of **1–9** in dilute solutions of CHCl₃ were recorded as well and the molar absorption coefficients were obtained and listed in Electronic Supplementary Information (ESI[†]). Obviously, the absorption of these mixed tetrapyrrole double-decker complexes was broadened and enhanced in the UV-Vis-NIR region over their respective reported mono(tetrapyrrole) and homoleptic bis(tetrapyrrole) complexes by the integration of both the porphyrin ligand and the phthalocyanine ligand.

The absorption spectrum of PDI shows three pronounced intense peaks at 522 nm, 486 nm, and 456 nm, and a weak peak at 431 nm, which corresponds to the 0–0, 0–1, 0–2, and 0–3 electronic transitions, respectively.^{17,41} PCBM exhibits an intense absorption at 328 nm, two weak peaks at 431 and 692 nm, and



Fig. 3 Absorption spectra of the yttrium double-decker complexes 8 and 9, as well as PDI and PCBM, in CH₂Cl₂.

a broad peak at 495 nm. The absorption peaks of PCBM in the visible region were often ignored previously.⁴²

Fig. S4 (see the ESI[†]) shows the absorption spectra of the mixtures of 1:PCBM (1 : 1, wt/wt), (1, 8 or 9):PDI (1 : 2, molar ratio) in CH₂Cl₂. The electronic absorption spectrum of the mixture is a linear superimposition of the individual components, indicating the absence of strong ground-state electronic interaction between the two components in these mixtures. This is also true for the mixtures of (2–7):PDI (1 : 2, molar ratio) in CH₂Cl₂ [Fig. S5 (ESI[†])]. The addition of PCBM significantly increased the absorption of complex 1 in the UV region. The introduction of PDI supplements the absorption of the double-deckers in the visible range, enabling the blend systems a broader band sunlight harvesting capability.

Fig. S6 and Fig. S7 (ESI[†]) shows the absorption spectra of the blend films of 1:PCBM, 1:PCBM:TiO_x, (1–9):PDI:TiO_x on ITO substrates. The broadening and shifting of the absorption peaks was observed compared with their absorption spectra in solution as shown in Fig. S4 and Fig. S5.[†] This is a result of molecular aggregation forming larger crystallites in the active layers. The blend films exhibit strong and full coverage of light absorption from 300 nm to longer than 1100 nm.

Steady-state emission

Photoluminescence was used to provide information about intramolecular and/or intermolecular charge or energy transfer processes in these sandwiched structures, which are of great help for understanding their photovoltaic behaviours in solar cells. Results reported thus far on the photoluminescence of sandwichtype tetrapyrrole rare-earth complexes still remain rare probably due to the very weak luminescence of such kinds of compounds associated with heavy atom effect (including strong static quenching or intersystem crossing) and strong electronic interaction between the neighboring tetrapyrrole ligands in the sandwiched molecules. According to Holten and Yamauchi and co-workers, homoleptic bis(porphyrinato) complexes of Ce, Y and La with either octaethylporphyrin or tetraphenylporphyrin ligand gave no photoluminescence.43,44 While weak photoluminescence was observed for either unsubstituted homoleptic bis(phthalocyaninato) europium complex Eu^{III}Pc₂,⁴⁵ or homobis[2.3.9.10.16.17.24.25-octakis(alkylthio)phthalocyanileptic nato] rare-earth complexes $M^{III}[Pc(SC_{16}H_{33})_8]_2$ (M = Eu, Tb, Lu),46 or heteroleptic bis(phthalocyaninato) rare-earth species $[M^{III}(Pc)(Pc')]-C_{60}$ (M = Sm, Eu, Lu).⁴⁷ In our recent work, no obvious steady-state emission was observed for the mixed-ring double-decker compound $Y^{III}H(TBPP)[Pc(\alpha - OC_4H_9)_8]$ (TBPP = tetrakis(4-butyl)porphyrinate) under either Soret band or Oband excitation.³⁵ The fluorescence of a metal-free porphyrin moiety attached through ester linkage at the meta or ortho position of one meso-phenyl group of porphyrin ligand in the mixed (porphyrinato)(phthalocyaninato) double-decker unit in triads is also effectively quenched by the double-decker unit.35 However, the fluorescence of their analogue with attachment at the para position is only partially quenched, revealing the effect of the position of porphyrin-substituent on the photophysical properties of the triads.³⁵ In the present case, no discernible steady-state emission was detected for the mixed (porphyrinato) (phthalocyaninato) complexes 1 and 4-8 under the characteristic Soret band or Q-band excitation of either the porphyrin or the phthalocyanine rings.

Interestingly, weak photoluminescence was observed for 2 and 3 under the excitation of either phthalocyanine Soret band at 324 nm or porphyrin Soret band at 420 nm. The fluorescence spectra of complexes 2-3 are compiled in Fig. S8 and Fig. S9 (ESI[†]). The fluorescence spectrum of 2 under the excitation wavelength of 324 nm bears two Soret band emissions at 388 and 434 nm, and one Q-band emission at 778 nm, all of which are phthalocyanine emissions. It is worth noting that the splitting of the Soret band emission can be ascribed to the spectrum overlap of the emission of the phthalocyanine ligand and the absorption of the porphyrin ligand, because the valley between the two peaks is exactly located at the strong Soret band absorption peak of the porphyrin ligand at 420 nm. The emission spectrum of 3 under the excitation wavelength of 324 nm showed similarity with that of 2, but with lower intensity. Under the excitation at 420 nm, very weak porphyrin Q-band emission was observed for 2-3, and the emission peaks are located at \sim 655 nm and \sim 705 nm. For complexes 1 and 4-7, their fluorescence signals became too trivial to be identified. It seems that along with the lanthanide contraction, the fluorescence quenching of the phthalocyanine and porphyrin emission becomes stronger. For the heteroleptic bis(phthalocyaninato) complex 9, only one weak Soret band emission at ~420 nm was observed under the Soret band excitation of 330 nm [Fig. S10 (ESI[†])]. Lanthanide ions are known to possess particular luminescent characteristics, however, no direct fluorescence related to the emission of lanthanide ions was observed in the visible range. It seems that in these sandwich-type lanthanide complexes, the metal ions sandwiched by two tetrapyrrole ligands can be considered to play only an indirect role on the luminescence of the whole molecules. It is likely that the rareearth metal ions affect the properties of the high π -conjugated sandwiched systems such as heteroleptic phthalocyaninato and

mixed (porphyrinato)(phthalocyaninato) metal compounds by tuning the distance between the adjacent tetrapyrrolic macrocycles.⁴⁵

Time-resolved fluorescence

In order to reveal the excitation behaviours of these sandwichtype tetrapyrrole complexes, ultrafast time-resolved fluorescence of 1-7 was investigated. Upon excitation at 420 nm which is corresponding to the Soret band absorption of the porphyrin ligand, the samples are excited to the second singlet state (S_2) of the porphyrin ligand within fs time scale. There are two possible channels for the energy relaxation of the S2 state within these complexes. First of all, the excitation energy may transfer to the first electronic state (S_1) of the porphyrin ligand by intra-system energy conversion within a time scale of tens of fs to few ps,48 and the S_1 may release energy through the intersystem crossing from the S_1 state to the triplet T_1 state within nanosecond time scale in the porphyrin ligand.⁴⁹ Since the porphyrin ligand is coupled to the phthalocyanine ligand by the metal center, the energy may also flow into the Q bands of phthalocynine ligand by means of ligand-to-ligand energy transfer,50 or flow into the rearearth metal center through ligand-to-metal energy transfer.45

In this work, the Q-band fluorescence dynamics at 655 nm of complexes 1-7 with excitation at 420 nm were measured and the fitting results are compiled in Table 1. As illustrated in Fig. 4, the Q-band emission of the porphyrin ligand in complexes 2, 6 and 7 quickly decayed within a time scale compared to the instrument response function of ~250 fs. Such a phenomenon was observed for mixed-ring double-decker complex $Y^{III}H(TBPP)[Pc(\alpha -$ OC₄H₉)₈] as well as in previous work.³⁵ An ultrafast decay component within ~ 250 fs was also observed for complexes 1 and 3-5. The ultrafast fluorescence decay, which has been reported for heteroleptic bis[(na)phthalocyaninato] samarium complex $[NcSm{Pc(OC_8H_{17})_8}]$ as well,¹⁷ suggests that the energy was relaxed through very fast channels in sandwich-type tetrapyrrole complexes. As the interplanar distance between the porphyrin ligand and the phthalocyanine ligand in mixed (porphyrinato)(phthalocyaninato) rare-earth complexes is only ~ 0.3 nm,³⁴ the ligand-to-ligand energy transfer, *i.e.* intramolecular energy transfer process from the excited porphyrin ligand to the phthalocyanine ligand, seems to be a reasonable assignment for this ultrafast decay based on their strong intramolecular π - π interactions. High amplitudes of this ultrafast decay for all these sandwich-type tetrapyrrole complexes were observed. It is likely

Table 1Multi-exponential fitting parameters for the fluorescencedynamics of the complexes 1–7 in CH_2Cl_2 with emission at 655 nm andexcitation at 420 nm

Complex	τ_1 (fs)	A1 (%)	τ_2 (ps)	$A_2 (\%)^a$	τ_3 (ps)	A ₃ (%)
2	250	98				
3	250	57.6	3.4	-19.3	26	21.1
4	250	57.8	1.7	-19.0	22	21.2
5	250	53.3	2.5	-22.3	31	22.4
1	250	45.7	2.8	-27.1	36	25.2
6	250	98	_			
7	250	98				

^{*a*} The sign of minus represents a rising behavior.



Fig. 4 Fluorescence dynamics of the complexes 1-7 in CH₂Cl₂ with emission at 655 nm and excitation at 420 nm. The red lines are plotted instrument response function and the blue ones are the fitted curves. The spectra are stacked in the order of **2-3-4-5-1-6-7**, following the ionic radius contraction sequence of the rare-earth(III) cations within these complexes.

that the exciton was delocalized between the macrocyclic ligands due to the π - π interactions.¹⁷

For the fluorescence dynamics of complexes 1 and 3–5, a relatively slow decay at time scale of 22–36 ps was found, as indicated by τ_3 in Table 1. This relatively long decay demonstrated different amplitude for complexes 1 and 3–5, implying that this process was associated with the rare-earth metal centers. This ~30 ps decay represents the inter-system crossing process from S₁ to T₁, which was reported in varied time scales from a few ps to a few ns in porphyrins.⁴⁸ Due to the heavy metal atom effect,⁵¹ this process is faster in the present case than that in metal-free porphyrins. Besides the ultrafast and the relatively slow decay processes, a 1.7–3.4 ps rising component appeared in the complexes of 1 and 3–5, as shown in both Fig. 4 and Table 1. This rising process might be originated from the intra-molecular inelastic collision.⁵² However, the possibility of thermal population of the S_1 states from the triplet states, as observed within other complexes,⁵³ could not be excluded as well.

From the discussion above, we could conclude that the photophysics of these sandwich tetrapyrrole complexes is associated with and can be tuned by the metal centers.

Device fabrication and characterization

All the complexes 1-9 with nice solubility were examined as the sunlight absorbers and electron donors in solution processed BHJ solar cells. The devices were constructed into structure of glass/ITO/PEDOT:PSS/active laver/LiF/Al, in which the active layer was made from the bis(tetrapyrrole) complexes (electron donors) blended with electron acceptors PCBM or PDI within TiO_x . The cell structure is illustrated in Fig. 5(a). The morphology of the active layer in BHJ solar cells is of vital importance for the photovoltaic performance of the devices. The interpenetrating networks of the donor and acceptor phases endowed the BHJ devices with a much larger interfacial area for more efficient dissociation of photo-induced excitons over those of bilayer heterojunction devices. The active layer surface morphology of selected optimized devices (without coating the LiF/Al electrode) has been investigated by atomic force microscopy (AFM).

A proposed working principle for this cell structure can be elucidated by Fig. 5(b). In this cell structure, the donor material (double-decker tetrapyrrole complex) harvests sunlight photons and generates excitons. The generated excitons diffuse to the donor/acceptor interface where charge separation occurs. Separated holes transport within donor material by hopping to the anode, while the separated electrons transport within the acceptor material by hopping to TiO_x and from there to the cathode.

Initially, PCBM was utilized as the electron acceptor during the cell fabrication. Fig. 6(a) shows the J-V curves for the solar cells made from 1 and PCBM. PCBM was mixed with complex 1 in weight ratios of 1:1, 2:1, 3:1 and 4:1. Devices with a variety of thickness of the active layer (10-200 nm) were fabricated by adjusting the speed of the spin-coating process. However, all the devices made from 1:PCBM without TiO_x matrix turned out with no photocurrent, which was out of our expectation. It was reported that the presence of very large aggregates (in µm) in the active layer of polymer solar cells can cause photovoltaic failure.54 However, the topography image [Fig. 7(a)] shows a relatively smooth film of 1:PCBM (1:1, wt/ wt) without distinct features, indicating no large scale (in µm) phase separation within the film, so that the formation of larger aggregates can be excluded.²¹ This was further supported by the phase image [Fig. 7(d)] of the film, in which the contrast in the nm scale represents areas of different material composition. In other words, only nanoscale phase separation was observed on the film surface. Nanoscale phase separation is needed for BHJ solar cells, since it provides large interfacial areas for efficient exciton dissociation, and organized nanodomains for more efficient carrier transport.55 There must be some reasons other than largearea phase separation inducing the photovoltaic failure of these devices. One possibility is the fatal back charge transfer induced by the decreased HOMO and increased LUMO of the bis



Fig. 5 (a) Device structure and (b) proposed working principle of the solar cells.

(tetrapyrrole) complexes compared to respective mono(tetrapyrrole) complexes.²⁵ Interestingly, when a TiO_x buffer layer was introduced in between the active layer and the aluminium (without LiF in this case), the cells became operational. An efficiency of 0.03% was obtained from cells made from 1:PCBM (1 : 1, wt/wt)/TiO_x, with V_{OC} of 0.10 V, and FF of 0.21. A dramatic improvement of the cell performance was further achieved by directly introducing the TiO_x into the active layer. Efficiency of 0.23% was obtained from the cell of 1:PCBM:TiO_x [the weight ratio of 1 to PCBM was 1 : 1, and the volume ratio of organics (*i.e.* both 1 and PDI) to inorganics (*i.e.* TiO_x) was 1 : 1], with an around threefold increment in the V_{OC} from 0.10 V to 0.42 V, a 58% increase in the short circuit current density (J_{SC}), and a 38% increase in the FF.

It is known that the back electron transfer dissipates the energy of the primary photoproducts (charges) as heat.⁵⁶ As illustrated by Marcus theory, ones may slow down any highly exergonic charge transfer reactions by factors of up to $\sim 10^4$ by operating the electron transfer reaction in the so-called "inverted region" even as the thermodynamic driving force of the reaction increases.⁵⁶ In these robust solar cells of double-decker complex: PCBM, there could be inverted regions. To discourage primary back electron transfer in the devices above, a secondary electron acceptor (TiO_x) was added in the redox chain. The electron

briefly lodged on the separated charges can be rapidly led away from the PCBM by a successive electron transfer to TiO_{y} . The addition of the TiO_x could induce the decrease of the Gibbs energy difference between the electron donor and the acceptor, as can significantly slow down the back charge transfer in the inverted region. In 2010, Cao and Luscombe and co-workers separately observed enhanced photovoltaic performance of polymer solar cells by fabricating P3HT:PCBM films with or within TiO₂ nanotubes, where they ascribed the efficiency rise to the improvement of charge collection and transportation, as well as improved electron mobility.^{15,16} Therefore, the enhanced J_{SC} of $1:PCBM:TiO_x$ cell may be attributed to the addition of the secondary acceptor TiO_x for blocking back electron transfer, and the efficient electron collection through the interpenetrating TiO_y. The FF increase benefits from the increase of the shunt resistance from 53 $\Omega \cdot cm^2$ to 260 $\Omega \cdot cm^2$, due to the suppression of the back transfer of electrons. It can be concluded that the secondary acceptor TiO_x plays an important role for improving cell performance and that the proposed operating principle is reliable.

Considering the need of more sufficient supplement of the absorption of these double-decker complexes in the visible region, the PDI which shows strong absorption at 420–540 nm was finally chosen as the electron acceptor instead of PCBM for



Fig. 6 J-V curves (empty: dark; filled: illuminated) of the cells of (a) glass/ITO/PEDOT:PSS/1:PCBM/TiO_x/Al, Glass/ITO/PEDOT:PSS/1:PCBM: TiO_x/LiF/Al, and (b) glass/ITO/PEDOT:PSS/double-decker complex (1–7):PDI:TiO_x/Al, under 1-sun AM 1.5G illumination.



Fig. 7 AFM (a–c) topography images and (d–f) phase images of the active layers of 1:PCBM (a & d), 6:PDI:TiO_x (b & e), and 9:PDI:TiO_x (c & f), respectively. Area: 0.5 μ m × 0.5 μ m.

the fabrication of the solar cells of 1–9. The active layer was composed of double-decker complex (1–9), PDI, and TiO_x. The ratio of the double-decker complex to PDI was fixed at 1 : 2 (molar ratio), and the ratio of organics (*i.e.* double-decker complexes and PDI) to inorganics (*i.e.* TiO_x) was controlled at 1 : 1 (volume ratio). During the cell fabrication, different active layer thicknesses were made by adjusting the speed of the spincasting process. Since a speed of 200–250 rpm for 40 s followed by 1000 rpm for 40 s afforded good devices in almost all the cases, we would like to mainly describe the cells fabricated under this spinning speed. This procedure gave active layers with thicknesses of 80–120 nm. At least 32 individual cells for each active material combination have been fabricated. Parameters of the best solar cells for each species are compiled in Table 2.

Fig. 7(b–c) and (e–f) exhibit the AFM topography and phase images of the films of 6:PDI:TiO_x and 9:PDI:TiO_x. The rootmean-square roughness of the films is 0.89 nm and 0.88 nm, respectively, indicating no large scale (in μ m) phase separation in the film.²¹ According to the phase image, phase separation within nanoscale occurred for the film, and the two distinct phases might be assigned to the organic and inorganic (TiO_x) phases, respectively.

Fig. 6(b) shows the J-V curves for the solar cells made from 1– 7 and PDI within the TiO_x matrix. For these mixed doubledecker complexes bearing a porphyrin ligand and an α -octosubstituted phthalocyanine ligand linked by coordination with different rare-earth metal centers, the open circuit voltage V_{OC} of their corresponding cells is in the range of 0.51-0.53 V. As it is known that the V_{OC} of heterojunction solar cells is determined by the offset of HOMO of the donor material and LUMO of the acceptor material,⁵⁷ similar $V_{\rm OC}$ values of these cells indicate similar HOMO energy levels of these double-decker complexes. For these devices with a relatively large area (0.36 cm^2) , the short circuit current densities J_{SC} are generally high, varying from 2.05 to 3.31 mA cm⁻². The FFs altered in the range of 0.43–0.57, but no obvious trend of FFs values was found along with this series of double-decker complexes. The origin of the altering FFs can be ascribed to the different series resistance R_s and different shunt resistance $R_{\rm sh}$ of the devices. The $R_{\rm s}$ of the devices varied in the range of 13–41 $\Omega \cdot cm^2$, while the corresponding $R_{\rm sh}$ changed in the range of 780–3400 $\Omega \cdot \text{cm}^2$. Higher R_{sh} indicates less back charge transfer (recombination). Film thickness, morphology, compositions, and structures of the components could affect these resistances. It is a challenge to precisely control the film

Table 2 Parameters of cells fabricated by double-decker tetrapyrrole complexes under 1-sun AM 1.5G illumination

Active layer	Cell area (cm ²)	$V_{\rm OC}$ (V)	$J_{\rm SC}~({ m mA~cm^{-2}})$	FF	η (%)	$R_{\rm s} \left(\Omega \cdot {\rm cm}^2 \right)$	$R_{\rm sh}$ (k $\Omega \cdot {\rm cm}^2$)
1:PCBM/TiO ^a	0.36	0.10	1.19	0.21	0.03	82	0.054
1:PCBM:TiO	0.36	0.42	1.88	0.29	0.23	140	0.26
2:PDI:TiO	0.36	0.53	2.57	0.53	0.72	22	1.2
3:PDI:TiO	0.36	0.53	2.92	0.53	0.82	15	1.5
4:PDI:TiO	0.36	0.52	3.31	0.43	0.74	41	0.78
5:PDI:TiO	0.36	0.53	2.27	0.56	0.67	13	3.4
1:PDI:TiO	0.36	0.53	2.16	0.55	0.63	31	2.7
6:PDI:TiO	0.36	0.52	2.74	0.46	0.66	37	2.5
7:PDI:TiO	0.36	0.51	2.05	0.57	0.59	25	3.3
8:PDI:TiO	0.36	0.46	1.64	0.49	0.37	32	1.5
9 :PDI:TiO _x	0.36	0.58	1.93	0.41	0.46	95	1.6

^a Solar cells have been prepared without depositing the LiF buffer layer.

thickness during the spin coating process. Even though the same concentration of the active materials solution and same spinning speed were adopted during the film fabrication, the film thickness still varied in the range of 80–120 nm. Varied film thickness might be the main probable reason for the variety of the series resistance. And larger amplitude of series resistances of these cells (up to several tens of $\Omega \cdot \text{cm}^2$) might be induced by low electron mobility of TiO_x. The shunt resistance may be mostly determined by the morphology of different cells. In the present work, the highest efficiency of 0.82% was accomplished with the europium counterpart, *i.e.* complex **3**. And the lutetium counterpart, *i.e.* complex **7**, showed the lowest efficiency of 0.59% due to the a little lower V_{OC} of 0.51 V and the lowest J_{SC} of 2.05 mA cm⁻² compared to solar cells made from other metal center counterparts.

The J-V curves of the solar cells made from the mixed (porphyrinato)(phthalocyaninato) yttrium double-decker complex 8 and the heteroleptic bis(phthalocyaninato) yttrium doubledecker complex 9, are presented in Fig. 8(a). For comparison, the J-V curve of the solar cell made from **3** is also exhibited in Fig. 8 (a). The $V_{\rm OC}$ is 0.53 V for the cell of **3**, 0.46 V for the cell of **8**, and 0.58 V for the cell of 9. For these observations, one of the reasons may be the different HOMO energy levels of the three complexes.⁵⁷ The J_{SC} values were 2.92, 1.64, and 1.93 mA cm⁻² for the cells of 3, 8, and 9, respectively, which directly resulted in a same trend of the conversion efficiencies of 0.82%, 0.37%, and 0.46% for these solar cells, respectively. High J_{SC} values may be ascribed to the broad absorption of these three complexes. The result was consistent with the measured IPCE of these three cells [Fig. 8(b)] in the region of 350-800 nm. The IPCE of the cells approximately follow the absorption spectra of thin films of constituent materials as shown in Fig. S6 and Fig. S7.† For complexes 3 and 8, the IPCE maxima were observed at around 430 and 415 nm, where the maximum of the Soret band absorption of the porphyrin macrocycle is located. IPCE at 650-800 nm mainly comes from the Q band absorption which shows more phthalocyanine character. The cell of 3 has IPCE > 7.8% in the range of 350-800 nm. The cell of 9 shows large IPCE at 605-800 nm, and the IPCE maximum is located at around 745 nm,

which is the location of the maximum of the Q band absorption of the phthalocyaninato complex. All the IPCE spectra did not fade away at $\lambda = 800$ nm, indicating the existence of photocurrent contribution at longer wavelengths. The significant contribution of PDI to IPCE at 450–540 nm in these cells has also distinctly revealed, indicating that the excitons generated in PDI can be effectively utilized by these cells as well.

In summary, the photovoltaic properties of bis(tetrapyrrole) complexes can be tuned either by changing the central metal ions or by varying the chemical structures of the macrocyclic ligands. The changing of the rare earth metal centers in the mixed (porphyrinato)(phthalocyaninato) complexes (1-7), caused a few to tens of nm blue or red shift of their absorption peaks, resulting in different light harvesting capability of these complexes at certain wavelengths to some extent. The rare-earth metal ions affect the energy transfer properties of these highly π -conjugated sandwiched systems by adjusting the distance between the adjacent tetrapyrrolic macrocycles. The fluorescence dynamics study revealed an ultra-fast energy transfer process between the macrocyclic ligands, and the generated excitons can be delocalized between the macrocycles due to the strong π - π interactions. The V_{OC} of complexes 1–7 showed much similarity, while the highest cell efficiency came from the most stable europium counterpart in this work. On the other hand, changing the substituent groups or the species of the ligands may affect the stable existence form (protonated or neutral or both) of these bis (tetrapyrrole) complexes which has been discussed in detail previously.³⁴ Complexes in protonated form and complexes in neutral form show much difference on their absorption profiles, and energy levels. All these can significantly change the spectral coverage and $V_{\rm OC}$ of the solar cell devices.

Conclusions

We presented photovoltaic applications of a series of new highly soluble sandwich-type protonated mixed (porphyrinato)(phthalocyaninato) double-decker complexes 1–7 with different rare earth metal centers. Comparative study was also carried out on a mixed (porphyrinato)(phthalocyaninato) yttrium complex 8,



Fig. 8 (a) J-V curves (empty: dark; filled: illuminated) and (b) incident photon to electron conversion efficiency (IPCE) of the cells of glass/ITO/ PEDOT:PSS/double-decker complex (3, 8, 9):PDI:TiO_x/Al, under 1-sun AM 1.5G illumination.

and a protonated heteroleptic bis(phthalocyaninato) yttrium complex 9. The addition of a secondary electron acceptor (TiO_x) significantly suppresses the back electron transfer between the bis (tetrapyrrole) complexes and the primary electron acceptor (PCBM or PDI). The applicability of the complexes 1-9 for broadband light harvesting bulk heterojunction solar cells has been ensured in spite of the difficulties to gain the exact HOMO/ LUMO energy levels of protonated tetrapyrrole double-decker complexes through electrochemical study.34,58 The solution processed bulk heterojunction solar cells of these bis(tetrapyrrole) complexes show efficiencies of up to 0.82%, comparable to some vacuum deposited devices of single-ring phthalocyanines. It has been concluded that variation of the macrocyclic ligand structures and the metal centers within double-decker bis(tetrapyrrole) complexes could tune their absorption, photophysical and photovoltaic properties. Further cell optimization is under investigation, and higher efficiency is anticipated.

Experimental section

General remarks

Dichloromethane (CH₂Cl₂) for spectroscopic studies was freshly distilled from CaH₂ under N₂. All other reagents and solvents were used as received from vendors. The compounds Y^{III}H (TClPP){Pc(α -OC₄H₉)₈} (1), Y^{III}(TClPP)(Pc) (8), Y^{III}H(Pc){Pc (α -OC₄H₉)₈} (9), and PDI were prepared according to the published procedures.^{17,32,34,38,58} The new complexes [M^{III}H(TClPP) {Pc(α -OC₄H₉)₈}] (M = Sm, Eu, Tb, Dy, Ho, Lu; 2–7) were prepared by a similar method as that of 1 (for detailed synthesis and characterization please see ESI†). PCBM was purchased from SES Research. Fig. 1 shows the schematic molecular structures of the double-decker complexes 1–9, PDI, and PCBM.

Absorption spectra were recorded on a Hitachi U-4100 spectrophotometer or on an Agilent 8453 UV-Visible Spectrophotometer. Steady-state emission spectra were recorded with an Edinburgh FS920 Fluorescence Spectrophotometer. Solutions for absorption and emission measurements were prepared using CH₂Cl₂ with a concentration of ~5.0 μ M for 1–9, PDI, and PCBM. Time-resolved fluorescence measurements for complexes 1–7 in solution were carried out by using a femtosecond fluorescence upconversion technique (for detailed measurements please see ESI⁺).

Device fabrication and measurement

Indium tin oxide (ITO) pre-coated glass with a sheet resistance of $8-12 \Omega$ /square was purchased from Delta Technologies. The ITO glass was cut into one inch by one inch pieces, and the ITO was patterned by etching with *aqua regia* vapour. The ITO glass substrates were then cleaned in an ultrasonic bath sequentially by hot detergent, hot deionized water, toluene, acetone, and isopropyl alcohol, each for 15 min, and then dried in a nitrogen stream, followed by O₂ plasma treatment for 10 min before use. Highly conductive poly(3,4-ethylenedioxylenethiophene):polystyrene sulfonic acid (PEDOT:PSS, Clevios P) thin layer was spin-coated (4000 rpm, 40 s) on the ITO substrates from an aqueous solution. The substrates were dried at 90 °C for 15 min under vacuum before spin-coating the photoactive layer. The solution of complex 1:PCBM blend was prepared by dissolving

a mixture of 1 and PCBM (1:1, wt/wt) in anhydrous CH₂Cl₂ at a concentration of 2 mg mL^{-1} . The solution of complex 1:PCBM: TiO_{x} was prepared by adding diethanolamine (32.7 mg mL⁻¹) and Ti(OC₄H₉)₄ (32.7 mg mL⁻¹) into the former solution. The complex (1-9):PDI:TiO_x blend solutions were prepared by dissolving a mixture of the corresponding complex and PDI (1:2, molar ratio) in anhydrous CH₂Cl₂ at 2 mg mL⁻¹, followed by addition of diethanolamine (32.7 mg mL⁻¹) and Ti(OC₄H₉)₄ (32.7 mg mL⁻¹). The active layer was deposited by spin-coating the CH₂Cl₂ solution of respective active materials on top of the PEDOT:PSS layer at 200-250 rotations per minute (rpm) for 40 s immediately followed by 1000 rpm for another 40 s. The devices were kept in air at room temperature for 2 h to ensure thorough conversion of the precursor $Ti(OC_4H_9)_4$ to TiO_x through hydrolysis. The devices were annealed at 120 °C under vacuum for 2 h, and then kept in vacuum at room temperature for another 12 h. Subsequently, an electrode including 1 nm thick LiF and 200 nm thick aluminium was deposited on the top by thermal evaporation in high vacuum ($< 5 \times 10^{-6}$ mbar). The active area of 0.36 cm² of the devices was defined by the area of deposited LiF/Al electrode through shadow mask.

The active layer morphology of some selected optimized devices (without coating the LiF/Al electrode) was investigated by atomic force microscopy (AFM) taken in air under ambient conditions using the intermittent contact mode on an Agilent 5500 AFM/SPM microscope. Current-voltage characteristics were measured using an Agilent 4155C semiconductor parameter analyzer. Devices were illuminated with an Oriel Xenon Arc Lamp Solar Simulator at an intensity of $\sim 100 \text{ mW cm}^{-2}$ (1-sun air mass 1.5 global illumination), which was calibrated with a Hamamatsu mono-crystalline Si cell standardized by National Renewable Energy Laboratory (NREL). Short circuit current density (J_{SC}) , open circuit voltage (V_{OC}) , and fill factor (FF) were obtained from the current density-voltage (J-V) curves. The conversion efficiency was calculated by $\eta = J_{\rm SC}V_{\rm OC}FF/P_{\rm in}$, where P_{in} is the incident power density; and FF is given by FF = $J_{\text{max}}V_{\text{max}}/J_{\text{SC}}V_{\text{OC}}$, where $J_{\text{max}}V_{\text{max}}$ is the maximum output power density of a solar cell. Incident photon to current conversion efficiency (IPCE) was recorded using Newport's QE/ IPCE Measurement Kit with a 74125 Oriel Cornerstone 260 1/4 m Monochromator.

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