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Introduction

DSSCs have drawn a broad interest as a cost-effective approach to convert solar energy into electricity.¹⁻¹⁰ The state-of-the-art power conversion efficiency of DSSCs has been increased very recently from $\sim 11\%$ for ruthenium complex based sensitizers to 12.3% for a donor- π -bridge-acceptor zinc porphyrin dye (YD2-o-C8).² In spite of this, ruthenium complexes are still the most widely used TiO₂ sensitizers in DSSCs so far.^{3,4} Due to the relatively high band gaps of these dyes, more than half of the total solar irradiance especially at wavelengths greater than 650 nm cannot be effectively harvested.^{3,5} In contrast, phthalocyanine dyes, as well-known low band gap absorbers with high chemical stability and tailorability, possess very strong absorption bands in the ultraviolet (UV) and red to near infrared (NIR) regions, along with a gap of very weak absorption in the visible region at 400 to 600 nm.³⁻⁹ This absorption gap allows efficient transmission of visible light without sacrifice of UV and red to NIR photon harvesting, and

Non-aggregated hyperbranched phthalocyanines: single molecular nanostructures for efficient semiopaque photovoltaics

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A series of single molecular nanostructured hyperbranched phthalocyanines, HBMPc-COOH (M = H₂, AlCl, Co, Cu, Zn), have been synthesized, characterized, and systematically studied as efficient semi-opaque sensitizers of TiO₂ by using ultraviolet-visible absorption, steady-state and femtosecond time-resolved fluorescence, cyclic voltammetry, current–voltage and photoelectric measurements. The inherent steric effect within these hyperbranched structures effectively suppresses the aggregation of phthalocyanine rings on TiO₂ surface, providing a facile approach for improving the photovoltaic performance of phthalocyanine-based dye sensitized solar cells (DSSCs). A power conversion efficiency of 1.15% along with a high incident photon to current conversion efficiency of 66.7% at 670 nm is achieved from HBZnPc-COOH sensitized solar cells. These results are consistent with findings from the femtosecond time-resolved fluorescence study, which reveals an ultrafast and efficient multi-phasic interfacial electron injection from both the Soret and *Q* bands to the conduction band of TiO₂. The changing of the metal centers dramatically affects the optical, photophysical, electrochemical, and photovoltaic properties of the hyperbranched phthalocyanine-based dyes for DSSC applications.

thus can be treated as a life window suitable for certain practical applications, such as semi-opaque solar panels to be equipped on building/greenhouse windows.^{6,11} Besides, this absorption window can be filled up through co-sensitization with other visible-light-harvesting $dye(s)^7$ or through chemical structure modification^{12–14} for broader spectral coverage toward more efficient DSSCs.

Many phthalocyanine sensitized solar cells have been developed in the last few years.³⁻⁹ However, their performance is not very impressive, mainly because of the strong tendency of phthalocyanines to aggregate on the TiO₂ surface and the lack of directionality of electron transfer in the excited state.^{4,5} Recently, it was found that asymmetrical structures with "push" and "pull" groups or with axially substituted ligands enable phthalocyanines to 1) reduce the aggregation on the TiO_2 surface, 2) tune the energy level of the excited state, and 3) provide intimate electronic coupling with the TiO₂ surface.³⁻⁸ As a result, good efficiencies of up to 4.6% have been obtained from asymmetrical phthalocyanine sensitized solar cells.⁵ The issues for asymmetrical phthalocyanines are their low synthetic yields and the difficulty in purification.³⁻⁸ On the other hand, single molecular nanostructured hyperbranched phthalocyanines with the desired advantages of facile synthesis and scalable processing procedures, have shown potential applications in solar cells,¹¹ organic light-emitting diodes,¹⁵ and highenergy density and pulsed capacitors¹⁶ in recent years. We

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expect that the use of hyperbranched structures can suppress the aggregation of phthalocyanines on the TiO_2 surface. To the best of our knowledge, there has been very little work regarding DSSC applications of hyperbranched phthalocyanine-based dyes. In this study, we synthesized a series of hyperbranched phthalocyanines, HBMPc-COOH ($M = H_2$, AlCl, Co, Cu, Zn; 1–5) (Scheme 1), as TiO₂ sensitizers in DSSCs. The optical, photophysical, electrochemical, and photovoltaic properties of these hyperbranched phthalocyanines were investigated.



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Experimental section

General remarks

N,N-Dimethylformamide (DMF) was distilled from anhydrous MgSO₄. All other reagents and solvents were used as received from Sigma-Aldrich. ¹H NMR spectra were recorded on a Varian 500 NMR Spectrometer or on a Bruker Avance 400 NMR Spectrometer in CDCl₃ or in DMSO-d₆. IR spectra were recorded in KBr pellets using a Nicolet 6700 FT-IR Spectrometer with a spectral resolution of 4 cm^{-1} . Mass spectra were taken on a Bruker TOF Mass Spectrometer or on an Applied Biosystems Voyager-DE Pro Biospectrometry Workstation Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) Mass Spectrometer (operating in both linear and reflector mode). Dithranol was used as the matrix in the measurements for 1-5. Gel Permeation Chromatography (GPC) data were collected using a Tosoh EcoSEC HLC-8320GPC equipped with a refractive index (RI) detector. Absorption spectra were recorded on an Agilent 8453 UV-visible Spectrophotometer. Steady-state fluorescence spectra were recorded with an Edinburgh FS920 Fluorescence Spectrophotometer. Solutions for absorption and fluorescence measurements were prepared using anhydrous DMF.

Synthesis

The hyperbranched phthalocyanines were prepared following the synthetic steps shown in Scheme 1.

Synthesis of 1,3-bis(3,4-dicyanophenoxy)benzene¹⁶

4-Nitrophthalonitrile (2.00 g, 11.6 mmol) and 0.64 g (5.8 mmol) of resorcinol (1,3-dihydroxybenzene) were dissolved in 30 mL of dimethyl sulfoxide (DMSO). Then 1.60 g (11.6 mmol) of potassium carbonate (K₂CO₃) was added into the flask, and the mixture was stirred at room temperature for 24 h. The mixture was poured into 600 mL of methanol/water (1/1, v/v)mixture and stirred for 30 min. The precipitate was collected by filtration, washed with 1000 mL of water, and dried under vacuum. The pure product was obtained by recrystallization in methanol. The powdery product was collected by filtration and dried under vacuum for 24 h, affording 1.77 g of 1,3-bis(3,4dicyanophenoxy)benzene. Yield: 84.1%. ¹H NMR (500 MHz, CDCl₃, δ (ppm)): 7.76-7.82 (d, 2H, -C₆H₄), 7.53-7.58 (t, 1H, - C_6H_4), 7.30–7.36 (m, 4H, $-C_6H_3$), 7.00–7.03 (m, 2H, $-C_6H_3$), 6.83–6.86 (t, 1H, $-C_6H_4$). MS: m/z 362.1 [Calcd. for $C_{22}H_{10}N_4O_2$: $[M]^+$ 362.3].

Synthesis of HBMPc-CN (M = H₂, AlCl, Co, Zn)

In general, 1,3-*bis*(3,4-dicyanophenoxy)benzene (~0.6 mmol) or its mixture with ~0.3 mmol of AlCl₃ or CoCl₂·6H₂O or ZnCl₂·*x*H₂O, was dissolved in 5 mL of 2-dimethylaminoethanol (DMAE), and then the mixture was refluxed for 75 min (for M = H₂, Zn) or 2 h (for M = AlCl, Co) under a slow stream of nitrogen. The mixture was poured into 100 mL of water/ methanol (10/1, v/v) mixture. The precipitate was collected by filtration, washed with 3 mol L⁻¹ HCl (this step was for M = AlCl only) and then with water, and dried under vacuum. After refluxing in methanol twice, the product was filtered and rinsed with cold methanol three times. The dark green/blue

powdery product was dried under vacuum, affording HBMPc-CN (M = H_2 , AlCl, Co, Zn) in yields of >85%.

For HBH₂Pc-CN: IR (KBr, cm⁻¹): 3400, 3300, 3050, 2210, 1720, 1600, 1480, 1280, 1220, 1120, 1080, 1020, 960, 800, 780, 720.

For HBAlClPc-CN: IR (KBr, cm⁻¹): 3440, 3050, 2210, 1750, 1600, 1480, 1280, 1220, 1120, 940, 780, 730.

For HBCoPc-CN: IR (KBr, cm⁻¹): 3400, 3050, 2210, 1750, 1600, 1480, 1280, 1220, 1120, 940, 780, 730.

For HBZnPc-CN: IR (KBr, cm⁻¹): 3400, 3060, 1710, 1600, 1490, 1400, 1360, 1280, 1210, 1120, 1050, 980, 822, 700.

Synthesis of HBCuPc-CN¹⁶

1,3-*bis*(3,4-Dicyanophenoxy)benzene (206.91 mg, 0.57 mmol) and 18.92 mg (0.19 mmol) of CuCl were dissolved in 5 mL of dimethylacetamide (DMAc), and then the mixture was stirred at 160 °C for 4 h. The mixture was poured into 100 mL of water. The precipitate was collected by filtration, washed with water, and dried under vacuum. After refluxing in methanol twice, the product was filtered and rinsed with cold methanol three times. The dark blue powdery product was dried under vacuum, affording 182.07 mg of HBCuPc-CN. IR (KBr, cm⁻¹): 3400, 3050, 2250, 1710, 1600, 1480, 1220, 1180, 1120, 1100, 980, 820, 750.

Synthesis of 1–5¹⁵

In general, HBMPc-CN (M = H₂, AlCl, Co, Cu, Zn) and potassium hydroxide (15 wt%) were dissolved in 12 mL of water/ethanol (1/1, v/v) mixed solvent. The mixture was refluxed for 24 h until the evolution of ammonia ceased. The blue clear solution was poured into 60 mL of water and the pH value of the solution was adjusted to 3-4. The dark blue precipitate was collected by filtration and rinsed with dilute HCl and then with water. Yield: >90%. GPC, MALDI-TOF MS, and UV-visible absorption extinction coefficients were used for estimating the molecular weight of the hyperbranched structures.¹⁶ Due to the limited solubility of 1-5 in tetrahydrofuran (THF), it was hard to obtain precisely their molecular weight information by GPC. GPC only provided the residual monomer information for 2-5. The GPC data for 1 revealed a broad molecular weight distribution with three to five rings on average in the structure. Several trials showed that dithranol was the best matrix for these samples, even though their solubility in acetonitrile was rather poor (in which the MALDI-TOF MS samples were prepared). Their MALDI-TOF MS spectra could not comprehensively reflect the actual molecular weight distribution either. However, the distinguishable ion peaks with largest molecular weight demonstrated that there were about four phthalocyanine rings within 2, 3, and 5. The MALDI-TOF MS spectra also revealed a quasi-Gaussian distribution of the molecular weights with intervals of one phthalocyanine ring's molecular weight and an approximate center at two/three rings for 2, 3, and 5. The observation above might be attributed to the different desorption degree and splitting/dissociation pathways of the hyperbranched structures. This made the assignments of the individual peaks difficult. However, the above results agreed well with the GPC ones for 1. It is worth noting that the MALDI-TOF MS spectra for 1 and 4 only showed the monomer information. This likely

originated from the poor desorption of the samples which possess strong intermolecular ring–ring interactions in the solid, including hydrogen bonding and π – π stacking of their extremely planar structures.¹⁷ Due to the possible presence of aggregates and observation errors, the UV-visible absorption extinction coefficient measurements¹⁶ of **1**–**5** in DMF demonstrated that there were five to eight phthalocyanine rings on average which were likely overestimated in their structures.

For 1: ¹H NMR (400 MHz, DMSO-d₆, δ (ppm)): 8.27–8.32 (d, HOOCPh–H), 7.95 (s, Pc–H), 7.44–7.57 (m, HOOCPh–H), 7.16– 7.23 (m, Pc–H), 6.86–6.98 (m, Ar–H). IR (KBr, cm⁻¹): 3300, 3080, 1880, 1800, 1720, 1600, 1480, 1280, 1220, 1120, 1090, 1020, 970, 880, 740. GPC (relative to polystyrene standards): $M_{\rm w} = 5748.8$, $M_{\rm n} = 3486.1$, $M_{\rm w}/M_{\rm n} = 1.65$.

For 2: ¹H NMR (400 MHz, DMSO-d₆, δ (ppm)): 8.00–8.20 (d, HOOCPh–H), 7.78 (s, Pc–H), 7.49–7.51 (d, HOOCPh–H), 7.48–7.49 (s, HOOCPh–H), 7.35–7.36 (d, Pc–H), 7.26–7.27 (d, Pc–H), 7.15–7.19 (dd, Ar–H), 7.03 (d, Ar–H), 6.97 (s, Ar–H), 6.92–6.93 (d, Ar–H). IR (KBr, cm⁻¹): 1880, 1800, 1720, 1610, 1490, 1280, 1220, 1125, 1080, 970, 895, 800, 760. MS: *m/z* 2033.50, 2361.95, 2781.94, 3200.90, 3649.47, 3915.29, 4832.10.

For 3: ¹H NMR (400 MHz, DMSO-d₆, δ (ppm)): 8.06–8.15 (br, HOOCPh–H), 7.55–7.65 (br, Pc–H), 7.5 (s, HOOCPh–H), 7.46–7.47 (d, HOOCPh–H), 7.23–7.24 (d, Pc–H), 7.16–7.19 (dd, Ar–H), 7.13–7.14 (d, Pc–H), 7.01–7.02 (d, Ar–H), 6.96 (s, Ar–H), 6.91–6.92 (d, Ar–H). IR (KBr, cm⁻¹): 3400, 3100, 1860, 1790, 1720, 1600, 1480, 1280, 1220, 1120, 1100, 980, 890, 800, 760. MS: *m*/*z* 2056.04, 2445.53, 2845.93, 3264.81, 4068.79, 4906.68.

For 4: ¹H NMR (400 MHz, DMSO-d₆, δ (ppm)): 8.21–8.23 (d, HOOCPh–H), 7.75 (s, Pc–H), 7.40–7.58 (m, HOOCPh–H), 7.31–7.36 (m, Pc–H), 7.15–7.20 (d, Pc–H), 7.03–7.11 (m, Ar–H), 6.89–6.91 (s, Ar–H). IR (KBr, cm⁻¹): 3400, 3080, 1900, 1810, 1730, 1600, 1480, 1420, 1280, 1220, 1140, 1100, 1060, 980, 900, 740.

For 5: ¹H NMR (400 MHz, DMSO-d₆, δ (ppm)): 12.7–14.2 (br, PhCOO–H), 7.80–7.85 (d, HOOCPh–H), 7.51 (s, HOOCPh–H), 7.49–7.50 (d, HOOCPh–H), 7.31–7.35 (dd, Ar–H), 7.27 (s, Pc–H), 7.19–7.20 (d, Pc–H), 7.15–7.17 (d, Pc–H), 7.03 (d, Ar–H), 6.98 (d, Ar–H), 6.96 (s, Ar–H). IR (KBr, cm⁻¹): 3400, 3200, 3050, 1870, 1795, 1710, 1600, 1480, 1280, 1220, 1120, 1050, 980, 890, 740. MS: *m*/*z* 2095.20, 2441.19, 2880.05, 3317.73, 4967.82.

Femtosecond time-resolved fluorescence measurements

A femtosecond fluorescence upconversion (FFU) technique was employed to investigate the fluorescence dynamics of the solutions of 1–5 and the films of $5/\text{TiO}_2$. The solutions were prepared with anhydrous, deoxygenated DMF at a concentration of $\sim 1.0 \text{ mg mL}^{-1}$. One-minute ultrasonication treatment was performed on the solutions to accelerate the dissolution process. The solutions were kept sealed and still at room temperature for at least 2 days. The clear solutions over the precipitate were then collected for test or for further use. Quartz plates were used as substrates to prepare the solid films of 5/TiO2. The quartz plates were cleaned in an ultrasonic bath sequentially by hot detergent, hot deionized water, acetone, and isopropyl alcohol, each for 10 min, and then dried by nitrogen flow. Transparent single-layered mesoporous TiO₂ ($\sim 5 \mu m$ thick) was coated by applying a nanoparticle TiO₂ paste (Ti-Nanoxide HT/SP, Solaronix) onto the quartz plates using a doctor blade technique. Scotch Magic tape with punched round holes was used as spacer to control the film thickness. The films were sintered at 100 °C for 15 min and then at 475 °C for 45 min. Right before the temperature decreased to 80 °C, the TiO₂ films were immersed into the dye solution and kept at room temperature for 12 h. The quartz plates were then taken out, flushed with anhydrous DMF followed with absolute ethanol, and dried by nitrogen flow and then under vacuum in an oven at ~50 °C for 6 h before test.

The measurements were carried out using the same system and procedures as described in detail in our previously reported work.^{14,18,19} The instrument response function (IRF) was estimated to be ~250 fs at full width at half maximum. The fluorescence data were fitted with a multi-exponential decay/rise model, in which the fluorescence signal F(t) can be theoretically expressed by a convolution of the IRF r(t) with a molecule-response function $f(\tau)$,

$$F(t) = \int_0^\infty r(t-\tau)f(\tau)\mathrm{d}\tau$$

where r(t) is a Gaussian function with laser pulse width and $f(\tau)$ is given by:

$$f(\tau) = \sum_{i} A_{i} \exp\left(-\frac{\tau}{\tau_{i}}\right)$$

where the factor A_i represents the relative weight (or amplitude) of corresponding component, whose sign can distinguish rising or decay process; and τ_i is the rising or decay time constant.

Electrochemical cyclic voltammetry measurements

Electrochemical cyclic voltammetry measurements were performed on a VersaSTAT 3 electrochemical working station (Princeton Applied Research). The cell comprised inlets for a platinum working electrode (MF-2013) of 1.6 mm in diameter and a platinum wire counter electrode. The reference electrode was an Ag/AgCl electrode (a 3.5 M KCl aqueous solution). Its potential was internally calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple [$E_{1/2}$ (Fc/Fc⁺) = +567 mV]. Typically, a 0.2 M solution of [NBu₄][PF₆] (tetrabutylammonium hexafluorophosphate) in anhydrous DMF containing sample (~3 mg mL⁻¹) was purged with nitrogen for at least 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 50 mV s⁻¹.

Device fabrication and characterization⁵⁻⁷

Fluorine-doped tin dioxide (FTO, with a thickness of ~400 nm and a sheet resistance of 8 Ω /sq) pre-coated glass purchased from Hartford Glass Co. was used as the substrate for cell fabrication. FTO glass substrates were cleaned using the same procedures as for quartz plates. Dye solutions were prepared at a concentration of 0.2 mg mL⁻¹ using the same procedures as for those prepared for the fluorescence dynamics test. A compact TiO₂ underlayer was deposited by spin coating at 3000 rotations per minute (RPM) for 30 s from a 0.1 M solution of titanium diisopropoxide *bis*(acetylacetonate) in ethanol on the FTO glass substrates followed by sintering first at 100 °C

for 15 min and then at 450 °C for 45 min. A transparent singleor double-layered mesoporous TiO₂ was coated by applying the nanoparticle TiO₂ paste (Ti-Nanoxide HT/SP, Solaronix) onto the compact TiO₂ using a doctor blade technique. Scotch Magic tape with punched round holes was used as spacer to control the film thickness. The film was sintered at 100 $^\circ \mathrm{C}$ for 15 min and then at 475 °C for 45 min. This method yielded a film thickness of $\sim\!5~\mu m$ for the single layer and $\sim\!10~\mu m$ for the double layer. A scattering TiO₂ layer ($\sim 4 \mu m$ thick) was made by doctor blading another anatase paste (WER4-O, Dyesol) on the mesoporous TiO₂ using the same procedures as above. The TiO_2 was sintered at 100 °C for 15 min and then at 500 °C for 45 min. The quality of these TiO₂ films for photoanodes was improved by further deposition of TiO₂ from aqueous TiCl₄ solution. A 0.2 M TiCl₄ aqueous solution was freshly diluted from a 1 M TiCl₄ stock solution which was prepared at 0 °C to prevent precipitation of TiO₂ due to the highly exothermic hydrolysis reaction. The dilute TiCl₄ solution was applied onto the electrodes (50 μ L cm⁻²). The electrodes were left overnight at room temperature in a closed chamber, spun at 1000 RPM for 20 s, and immediately washed with distilled water while wet. After further rinsing with absolute ethanol, the TiO₂ electrodes were dried by nitrogen flow. After being fired again at 450 °C for 40 min in air, and right before the temperature of the TiO₂ electrodes decreased to 80 °C, these films were immersed into the dye solutions and kept at room temperature for 12 h. The films were taken out, flushed with anhydrous DMF followed with absolute ethanol, and dried by nitrogen flow. The photoanodes were then dried under vacuum in an oven at ~ 50 °C for 6 h. An electrolyte solution was prepared by dissolving 0.6 M 1-butyl-3-methylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M tert-butylpyridine in a 15/85 (v/v) mixture of valeronitrile and acetonitrile. Counter electrodes were prepared by sputter deposition of 40 nm thick films of Pt on pre-cleaned FTO glass substrates using a CrC-150 Sputtering System. A parafilm mask was used as both spacer and sealing material for the two electrodes. The two electrodes were connected by the parafilm mask at 80 °C in air on a hotplate platform. The electrolyte solution was injected from two pre-cut channels of the mask and the final cells were sealed by hot glue. The active area was 0.31 cm² for all the cells.

Current-voltage characteristics were measured using an Agilent 4155C Semiconductor Parameter Analyzer under 1 sun air mass (AM) 1.5 global illumination. 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.

Results and discussion

Steady-state absorption and fluorescence

The steady-state absorption and fluorescence spectra of 1-5 were recorded in anhydrous DMF and the data are compiled in Table 1. As a quick characterization, the absorption spectra of 1-5 (Fig. 1) displayed intense *Q*-band peaks at 666 to 699 nm

Table 1 Steady-state UV-visible absorption and fluorescence data for $1\!-\!5$ in anhydrous DMF

Sample	λ_{\max}^{a} (nm)					$\lambda_{\rm em}{}^{b}$ (nm)			
1	330	_	615	634	666	699		707	784
2	355	363	616	_	686	_	_	699	765
3	339	_	603	_	668	_	427	706	_
4	342	_	612	_	676	_	433	_	_
5	352	_	615	_	676	_	_	690	755
				1					

^{*a*} Absorption peak maximum. ^{*b*} Emission peak maximum.

with medium vibronic bands at 606 to 616 nm, all of which are corresponding to the characteristic π - π * transition of monomeric phthalocyanines.^{20–22} Furthermore, the position of both Soret and Q bands absorption peaks of 1-5 showed dependence on the nature of the central metal ions. A red shift of both the Soret and Q bands was observed when the metal center was changed in the sequence of Co-Cu-Zn-AlCl. A same trend was previously observed by Liu et al. from a series of water-soluble sodium salts of sulfonated phthalocyanines $[MPc(SO_3Na)_4, M = H_2, AlCl, Co, Cu, Zn]^{21}$ The sharpness of the absorption peaks indicates the non-aggregating nature of the phthalocyanine rings in these hyperbranched structures in DMF solution.²² With strong absorption in the UV and red region, 1-5 showed a window with very weak absorption at from 400 to 600 nm, which may be utilized for some practical photovoltaic applications, such as solar cells for a greenhouse.^{6,11} This absorption gap may also be complemented by other visible light harvesting materials for more efficient photovoltaic cells.⁷

Steady-state fluorescence was used to provide information for understanding the photo-generation of charge carriers and intra/intermolecular energy transfers within 1-5.¹⁴ Fig. 2 shows the emission and excitation spectra of 1-5. Upon excitation at the Soret band of 400 nm, 1, 2, and 5 individually exhibited a strong *Q* band emission peak at 690 to 707 nm along with a medium *Q* band emission peak at 755 to 784 nm. The *Q* band emission for phthalocyanines corresponds to the



Fig. 1 UV-visible absorption spectra (normalized to their own *Q* band maxima) of **1–5** in anhydrous DMF.



Fig. 2 Fluorescence spectra of **1–5** in anhydrous DMF. Excitation spectra, if shown, were normalized to the maxima of their own emission spectra under the excitation of Soret absorption peak.

 S_1 - S_0 transition. We can conclude that the energy from the Soret band excitation was efficiently transferred to the *Q* bands for **1**, **2**, and **5**. Under the same conditions, not only a weak *Q* band emission peak at 706 nm but also a broad weak Soret band emission peak at ~427 nm was observed for **3**. In comparison to **1**, **2**, and **5**, this excitation seems more localized on the Soret band, as may be attributed to the electron-withdrawing properties of the Co center. Only a broad, weak Soret band emission peak at ~433 nm was detected for **4**, which is in line with previously published results for typical CuPc.²³ There was a very small portion of the energy from the Soret band excitation contributing to the broad, weak emission of **4**. Most of the excitation energy was transferred to the *Q* band and led away by a very quick channel, *i.e.* the intersystem crossing (ISC) from singlet state (S₁) to triplet state

(T₁). This is consistent with the findings from the femtosecond time-resolved fluorescence measurements. The sharpness of the emission peaks indicates that it is the individual phthalocyanine ring which fluoresces.²⁴ The very strong Q band emission peaks for **1**, **2**, and **5** indicate that each phthalocyanine ring is isolated from each other in one hyperbranched molecule, which inhibits quenching due to self-assembly.²⁵ From Fig. 2, it was further noted that the Q band emissions showed no excitation dependence, and that the excitation spectra at corresponding emission maxima approximately resemble the absorption spectra. Besides, the excitation spectra profiles did not vary with the detecting emission wavelengths. These results confirmed the fact that there was a single emitting species, *i.e.* the phthalocyanine core, in the hyperbranched structures.²⁵

There is a great difference in the fluorescence spectra of 4 [a CuPc], from those of the others. Q band emission of CuPc derived from upconversion transfer resulting from a plasmonenhanced triplet-triplet annihilation of molecules was once observed for a CuPc film deposited on Au (111) using tunneling electrons from a scanning tunneling microscope.²³ Other than this single observation under very unusual conditions, Q band emission of CuPc has never been observed by common emission analysis methods such as the steadystate fluorescence spectroscopy due to the extremely low intrinsic Q band fluorescence quantum yield from a CuPc molecule.^{23,26} The fluorescence lifetimes of common fluorescent compounds including H2Pc, AlPc, ZnPc, are at the time scale of 0.5 to 20 ns.²⁷⁻²⁹ Consistent with previous results, strong Q band emission was detected for 1, 2, and 5 in solution by the steady-state fluorescence spectroscopy. Al and Zn are both non-transition metals without incomplete d shells, while Co and Cu are transition metals with incomplete d shells. When Co^{2+} or Cu^{2+} is coordinated with the four pyrrole nitrogen atoms within the phthalocyanine ligand, the d orbital electrons get involved in the electronic interaction between the metal and the phthalocyanine π -conjugated system. For CuPc, the open-shell paramagnetic Cu²⁺ ion facilitates spin-orbit coupling. As a result, CuPc exhibits fast ISC with a time scale of subpicoseconds to picoseconds,^{11,30} and thus very short Q band fluorescence lifetime and very small fluorescence quantum yield. In the present case, the Q band fluorescence lifetime of 4 was determined to be 0.75 ps (corresponding to the ISC from S_1 to T_1) by the femtosecond time-resolved fluorescence method, which is three to four orders of magnitude shorter than that of common fluorescent species and thus beyond the detection capability of steady-state fluorescence spectroscopy.²⁷ This is the reason for the absence of steady-state Q band emission for 4. As for 3 [a CoPc], the Q band fluorescence lifetime of CoPc has been reported to be ~ 2.1 ps,³¹ which is longer than the Q band fluorescence lifetime of 4, but much shorter than that of other metal centered phthalocyanines (1, 2, and 5), therefore, very weak steady-state fluorescence (both Soret band and Q band) was observed for 4.

It is worth noting that the absence of Q band emission (S₁–S₀ transition) in steady-state fluorescence spectra doesn't have to mean the absence of S₂–S₁ transition. In fact, the Q band

emission signals of **4** have been detected by the following femtosecond time-resolved fluorescence measurements.

Femtosecond time-resolved fluorescence

FFU as a powerful technique has been widely used to investigate ultrafast processes, including excitation energy migration,^{11,13,14,18,19,32,33} charge separation and transfer,^{11,18} and interfacial electron injection.^{11,32} In the present work, we employed the FFU system to reveal the dynamics of ultrafast photo-induced initial processes of **1**–**5** in solution and the interfacial electron injection processes at the 5/TiO₂ interface.

Both the Soret and *Q* bands fluorescence dynamics of 1-5 in solution were investigated under the excitation of 400 nm. All the fluorescence data were fitted well with bi-exponential decays or decay/rise. Fig. 3 illustrates the Soret band fluorescence dynamics of 1-5 with excitation at 400 nm and

emission at 480 nm, and the fitting parameters are compiled in Table 2. As indicated by τ_1 in Table 2, the ultrafast decay component of 102-494 fs with large amplitude for 1-5 is assigned to intrasystem energy conversion from the excited electronic state S_2 to S_1 (Soret band to Q band energy transfer),¹¹ which might be coupled with intrasystem energy vibrational redistribution^{18,33} in the present cases. It is worth noting that the conversion rate $(1/\tau_1)$ for the hyperbranched metal-free phthalocyanine 1, is the slowest, while this rate for AlCl, Co, Cu and Zn centered hyperbranched phthalocyanines 1-5 is at least 1.8 times as fast as that of 1. It seems that the presence of metal centers in the hyperbranched phthalocyanines can significantly accelerate the ultrafast energy transfer process from the Soret band to the Q band. The slow decay τ_2 in the time scale of 7.26–9.43 ps for 1–5 with small amplitude might be designated to the lifetime of Soret band fluorescence.



Fig. 3 Soret band fluorescence dynamics of 1–5 in anhydrous DMF with excitation at 400 nm and emission at 480 nm. The red lines are the plotted IRF and the blue ones are the fitted curves.

 Table 2 Bi-exponential fitting parameters for the Soret band fluorescence

 dynamics of 1–5 in anhydrous DMF with excitation at 400 nm and emission at 480 nm

	2 (1)	112 (70)
72.4	7.26	27.6
66.7	8.78	33.3
98.8	8.20	1.22
85.9	9.43	14.1
83.3	8.58	16.7
	72.4 66.7 98.8 85.9 83.3	72.47.2666.78.7898.88.2085.99.4383.38.58

However, the possibility of excitation energy transfer (EET) which occurs between segments, and thermal equilibrium by energy exchange with the solvent, in a time scale of a few ps to several tens of ps,^{18,33,34} could not be excluded. The EET process may be interpreted by a resonance energy transfer model between the weakly coupled segments.³³

Fig. 4 displays the Q band fluorescence dynamics of 1–5 except 3 with excitation at 400 nm, and the fitting parameters are listed in Table 3. It is worth noting that there were extremely weak emission signals in the region of from 700 to 800 nm (Q band emission) with unidentified characteristics for HBCoPc-COOH (3), as might further prove that the excitation is more localized on the Soret band. Also, there might be ultrafast energy relaxation in very quick channels within the IRF or other mechanisms induced by a high-intensity laser beam such as the possible metal-to-ligand charge transfer process in 3. For the Q band emission of other

Table 3 Bi-exponential fitting parameters for the *Q*-band fluorescence dynamics of **1–5** in anhydrous DMF with excitation at 400 nm

Sample	τ_1 (fs)	$A_1 (\%)^a$	τ_2 (ps)	A_2 (%)
$egin{array}{c} 1^b \ 2^b \end{array}$	36.0 156	$-45.4 \\ -53.2$	296 196	54.6 46.8
$3^{b,c}$ 4^d 5^d	 32.0 70.0	-66.0 -44.2	 0.75 66.0	 34.0 55.8

 a The minus sign represents a rising behavior. b With emission at 700 nm. c No emission signal was detected. d With emission at 690 nm.

hyperbranched phthalocyanines (1–5 except 3), the ultrafast rising time of 32.0 to 156 fs represents the intrasystem conversion from the Soret band to the *Q* band, whose time scale should be consistent with the ultrafast decay time for Soret band emission. For the hyperbranched copper phthalocyanine (4), a relatively slow decay (τ_2) of 0.75 ps appeared immediately after the rising time for *Q* band emission. This relaxation path can be assigned to the ISC from S₁ to T₁. This is in good agreement with the results for another hyperbranched copper phthalocyanine in solution.¹¹ For the H₂, AlCl and Zn centered hyperbranched phthalocyanines (1, 2, and 5) in solution, a relatively slow decay τ_2 at the time scale of 66–296 ps appeared in their *Q* band emission dynamics right after the ultrafast rising time. It can be attributed to the relaxation of the first singlet state, as the existence of a lower



Fig. 4 Q band fluorescence dynamics of 1–5 except 3 in anhydrous DMF with excitation at 400 nm. The red lines are the plotted IRF and the blue ones are the fitted curves.



Fig. 5 Anisotropy decay profiles for the Q-band emissions of 1, 2 and 5 in anhydrous DMF with excitation at 400 nm. The red lines are the plotted IRF.

excited singlet state for **1**, **2**, and **5** has been confirmed by their steady-state emission peaks at longer wavelengths as shown in Fig. 2. This process might include the EET process.^{18,33} Compared to the metal-free hyperbranched phthalocyanine **1**, the existence of the metal centers of AlCl and Zn accelerated this relaxation process.

As shown in Fig. 5, the anisotropy for the *Q* band fluorescence dynamics of **1**, **2** and **5** is almost a constant of ~ 0.2 , which indicates the symmetry breaking in these delocalized systems and that the excitation of one ring might be transferred to other rings.¹⁷ Otherwise, with the exciton

located on one ring, a residual anisotropy value of 0.1 in such a planar structure should be expected.^{17,35} This provides evidence for the electron hopping process in these hyperbranched systems, because the symmetry breaking could possibly induce more traps.¹⁷

The femtosecond time-resolved fluorescence of $5/\text{TiO}_2$ film was also investigated to reveal the interfacial electron injection kinetics. Under the Soret band excitation at 400 nm, both the Soret and *Q* bands fluorescence dynamics of $5/\text{TiO}_2$ film were recorded. The fluorescence data were fitted well with biexponential decays. Fig. 6 shows both the Soret band (480 nm)



Fig. 6 Fluorescence dynamics of 5/TiO₂ film with excitation at 400 nm. The red lines are the plotted IRF and the blue ones are the fitted curves.

 $Table \; 4$ Bi-exponential fitting parameters for the fluorescence dynamics of 5/ TiO_2 film with excitation at 400 nm

Emission wavelength	τ_1 (fs)	$A_1 (\%)^a$	$\tau_2 \text{ (ps)}$	A_2 (%)
480 nm	241	86	3.1	14
690 nm	454	76	3.6	24

and Q band (690 nm) fluorescence decay profiles of 5/TiO₂, and the fitting parameters are compiled in Table 4. For the Soret band fluorescence dynamics, the ultrafast decay component of 241 fs with large amplitude, as indicated by τ_1 in Table 4, is assigned to the intrasystem energy conversion from the excited electronic state S_2 to S_1 ,¹¹ which might be coupled with intrasystem energy vibrational redistribution.^{18,33} It is worth noting that the conversion rate $(1/\tau_1)$ is faster than that for 5 in solution, indicating a possibility of the co-existence of the energy migration from S_2 to S_1 and the energy migration from S_2 directly to the conduction band of TiO₂.¹¹ The slow decay τ_2 in a time scale of 3.1 ps with small amplitude might still be designated to the lifetime of Soret band fluorescence or EET process, which is faster than that in solution as well. For the Q band fluorescence dynamics, the ultrafast decay process (τ_1) in a time scale of 454 fs can be attributed to the interfacial electron injection from the S1 state of the hyperbranched phthalocyanine 5 to the conduction band of TiO_2 . The relatively slow decay τ_2 appeared in the time scale of 3.6 ps, which is much faster than that in solution, can still be assigned to the relaxation of the first singlet state which might be coupled with EET process between the rings. In summary, efficient and ultrafast multi-phasic electron injection from both the Soret and Q bands of the hyperbranched zinc phthalocyanine 5 to the conduction band of TiO₂ was demonstrated.

Electrochemical properties

The electrochemical redox behaviors of 1–5 in anhydrous DMF solution were investigated by cyclic voltammetry (CV). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of 1–5 as well as their band gaps were determined by CV in associate with their UV-visible absorption spectra (Fig. 1) in DMF. All the redox data are compiled in Table 5. All the five hyperbranched phthalocyanines displayed reversible n-doping/de-doping (reduction/reoxidation) processes in the negative potential

region, and the reductive cyclic voltammograms of 1-5 are shown in Fig. 7. Note that no remarkable oxidation waves were observed in the positive potential range, and instead, only small bumps in the positive potential range were found. The positions of these small bumps were in approximate agreement with the corresponding onset oxidation potentials which were estimated from a combined analysis of the onset reduction potentials with the optical band gaps of 1-5. The much smaller oxidation waves (bumps) on the cyclic voltammograms may be tentatively interpreted by the hyperbranched molecular structure of 1-5. The phthalocyanine rings in one molecule of 1-5 were surrounded by non-conjugated bulky substituents. As is known, the electrochemical oxidization is a process occurring at the surface of the electrode.³⁶ It might be difficult for the phthalocyanine cores to reach to the electrode and get oxidized there.36

For DSSCs, HOMO/LUMO energy levels of the dyes are required to be appropriate in order for both effective electron injection to the conduction band of TiO₂ and effective electron acceptance from the iodide/triiodide (I^{-}/I_{3}^{-}) electrolyte.^{3,37} For efficient electron injection into the conduction band of TiO₂, the LUMO energy levels of the dyes should be sufficiently higher than the conduction band edge of TiO₂.^{3,37} While for efficient dye regeneration, the HOMO energy levels of the dyes should be sufficiently lower than the potential of the electrolyte redox.^{3,37} The hyperbranched phthalocyanines 1-5 displayed LUMO energy levels of -3.58 to -3.86 eV, which are all higher than the conduction band edge (-4.2 eV) of TiO₂,³⁸ demonstrating the possibility of efficient electron injection. On the other hand, the HOMO energy levels of 1-5 are in the range of -5.32 to -5.63 eV, all of which are lower than the redox potential of I^{-}/I_{3}^{-} (reported values range from -4.84 to -4.97 eV in organic solvents¹⁰), ensuring the possibility of efficient electron transfer from the electrolyte.

Photovoltaic performance

As the HOMO/LUMO energy levels of 1–5 were determined to be appropriate for charge extraction, all the five hyperbranched phthalocyanines were used as sensitizers of TiO₂ in DSSCs. The *J*–*V* curves of the solar cells were illustrated in Fig. 8 and Fig. 9(a). Table 6 summarizes the *J*–*V* characteristics, including the short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (η) of the DSSCs under 1 sun AM 1.5 G illumination.

 Table 5 Optical and redox properties of 1–5 in anhydrous DMF

Sample	$\lambda_{\text{onset}}^{\text{abs}}(\text{nm})$	$E_{\rm g}^{\rm opt}$ (eV) ^{<i>a</i>}	$E_{\rm red}^{\rm onset} ({\rm V})^b$	$E_{\rm ox}^{\rm onset}$ (V) ^c	$HOMO^d$ (eV)	$LUMO^{e}$ (eV)
1	722	1.72	-1.20	+0.52	-5.32	-3.60
2	705	1.76	-1.17	+0.59	-5.39	-3.63
3	691	1.80	-1.22	+0.58	-5.38	-3.58
4	698	1.78	-1.20	+0.58	-5.38	-3.60
5	699	1.77	-0.94	+0.83	-5.63	-3.86
5	699	1.77	-0.94	+0.83	-5.63	-3.86

^{*a*} The optical band gap was estimated from UV-visible absorption onset by $E_g^{opt} = 1240/\lambda_{onset}^{abs}$ (eV). ^{*b*} Onset reduction potential *vs.* Fc/Fc⁺. ^{*c*} Onset oxidation potential was calculated by $E_{ox}^{onset} = E_{red}^{onset} + E_g^{opt}$. ^{*d*} HOMO was calculated by HOMO = $-(E_{ox}^{onset} + 4.8)$ (eV). ^{*e*} LUMO was calculated by LUMO = $-(E_{red}^{onset} + 4.8)$ (eV).



Fig. 7 Reductive cyclic voltammograms of 1-5 in anhydrous DMF.

The hyperbranched zinc phthalocyanine (5) was first fabricated into DSSCs because 5 has been characterized the most comprehensively, especially by the femtosecond timeresolved fluorescence study of the $5/\text{TiO}_2$ films. The fluorescence dynamics study revealed ultrafast and efficient multiphasic electron injection from 5 to TiO₂, from which a decent photovoltaic performance of 5 in DSSCs was anticipated. The device structure optimization was performed on 5 and then the optimized structure was applied to all other hyperbranched phthalocyanines. Therefore, it appears necessary to describe the performance of 5 first. To facilitate the elucidation of the effect of cell structure on the cell performance, the *J*-*V* curves of 5 are shown in Fig. 8. Devices with a simplified TiO₂ electrode, consisting of a ~100 nm thick compact layer



Fig. 8 (a) *J–V* curves (empty: dark; filled: illuminated) of the DSSCs of **5** fabricated (a) with a single-layered mesoporous TiO₂ (~5 µm), and without the scattering TiO₂ layer; (b) with a double-layered mesoporous TiO₂ (~10 µm) and a scattering TiO₂ layer, under 1 sun AM 1.5 G illumination.

and a 5 µm thick mesoporous layer, exhibited a moderate efficiency of 0.832%, with a $V_{\rm OC}$ of 0.53 V, a $J_{\rm SC}$ of 2.05 mA cm^{-2} , and a FF of 0.767. For further optimization, devices with a comprehensive TiO₂ electrode consisting of a ~ 100 nm thick compact layer, a 10 µm thick mesoporous layer, and a 4 µm thick scattering layer, with TiCl₄ treatment, were fabricated for dye-soaking. Compared to the simplified cell structure, the comprehensive cell structure had a thicker mesoporous TiO₂ layer (10 μ m), and one extra scattering TiO₂ layer (particle size ~400 nm). Moreover, the TiO_2 film in the comprehensive structure was treated with TiCl₄ solution. A higher efficiency of 1.15% was obtained with a $V_{\rm OC}$ of 0.491 V, a $J_{\rm SC}$ of 3.20 mA cm^{-2} , and an only slightly lower FF of 0.731. The impressive 56% increase of the I_{SC} was attributed to the doubling of the thickness of the mesoporous TiO₂ layer which offered more dye loading, as well as to the enhancement of light absorption resulting from the addition of the TiO₂ light scattering layer.³⁹ A 0.04 V decrease of the $V_{\rm OC}$ was observed as the thickness of the TiO₂ film was increased. This effect has been widely observed for DSSCs based on TiO₂ nanoparticles.³⁸ It is due to the enlargement of the surface area which provides additional charge-recombination sites, and the enhancement of the dark current which results from the direct reduction of the electrolyte by the conduction band electrons of TiO2.40,41 It is known that the major problem for using phthalocyanine dyes to sensitize TiO₂ is their intrinsic tendency toward aggregation.⁴² In comparison to a monolayer of dye molecules that is directly connected to TiO2 surface, aggregated phthalocyanines are less effective to inject electrons to TiO2.42 Moreover, the excess of outer dye molecules induce inefficient light absorption.⁴² The aggregation dramatically reduces the power conversion efficiency of phthalocyanine-based DSSCs.42 In the present cases, both the efficiency and fill factor are as high as those of some monomeric zinc phthalocyanine-sensitized solar cells with 3α,7α-dihydroxy-5β-cholonic acid (CDCA) as a co-adsorbent, indicating the non-aggregating nature of the



Fig. 9 (a) J–V curves (empty: dark; filled: illuminated) and (b) incident photon to current conversion efficiencies (IPCE) of the DSSCs of 1–5 fabricated with a doublelayered mesoporous TiO₂ and a scattering TiO₂ layer under 1 sun AM 1.5 G illumination.

hyperbranched phthalocyanine molecules on the surface of TiO_2 .⁹

The comprehensive cell structure which yielded relatively high power conversion efficiency for 5 was adopted for the fabrication of DSSCs of all other hyperbranched phthalocyanines 1-4. Fig. 9(a) summarizes the J-V curves of the DSSCs fabricated from 1-5 with the same comprehensive cell structure. Cells of the hyperbranched metal-free phthalocyanine 1 showed an efficiency of 0.234%, with a $V_{\rm OC}$ of 0.434 V, a $J_{\rm SC}$ of 0.837 mA cm⁻², and a FF of 0.644. In contrast, DSSCs fabricated from a previously reported sterically hindered monomeric metal-free phthalocyanine dye showed no photocurrent due to a low excited singlet state compared with the conduction band of TiO2.43 Cells of the hyperbranched aluminum phthalocyanine chloride 2 displayed an efficiency of 0.294%, with a V_{OC} of 0.424 V, a J_{SC} of 1.05 mA cm⁻², and a FF of 0.662. Cells of the hyperbranched cobalt phthalocyanine 3 displayed a very low efficiency of 0.096%, with a $V_{\rm OC}$ of 0.324 V, a $J_{\rm SC}$ of 0.425 mA cm⁻², and a FF of 0.700. Cells of the hyperbranched copper phthalocyanine 4 exhibited an efficiency of 0.233%, with a $V_{\rm OC}$ of 0.420 V, a $J_{\rm SC}$ of 0.805 mA cm^{-2} , and a FF of 0.688. The generally high fill factors, ranging from 0.644 to 0.731 for cells of 1-5, are likely the

Table 6 Parameters of the DSSCs fabricated with 1–5 and measured under 1 sun AM 1.5 G illumination

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Dye	Cell area (cm²)	$V_{\rm OC}$ (V)	$J_{ m SC} \ (m mA\ cm^{-2})$	FF	η (%)	IPCE _{max} (%)
1 ^{<i>a</i>}	0.312	0.434	0.837	0.644	0.234	6.28
2^a	0.312	0.424	1.05	0.662	0.294	23.5
3 ^{<i>a</i>}	0.312	0.324	0.425	0.700	0.096	5.16
4 ^{<i>a</i>}	0.312	0.420	0.805	0.688	0.233	8.72
5 ^{<i>a</i>}	0.312	0.491	3.20	0.731	1.15	66.7
5^{b}	0.312	0.530	2.05	0.767	0.832	

 a Cells have been fabricated with a double-layered mesoporous TiO₂ (~10 µm) and a scattering TiO₂ layer. b Cells have been fabricated with a single-layered mesoporous TiO₂ (~5 µm) and without a scattering TiO₂ layer.

consequence of the successful suppression of the aggregation tendency of phthalocyanine rings on TiO₂ surface by the hyperbranched structure via non-conjugated bulky substituents.⁵ The non-conjugated bulky substituents surrounding the phthalocyanine rings may block their interaction with I₃⁻ to some extent, resulting in a limited recombination enhancement compared to N719 dye.⁵ The V_{OC} s of these solar cells varied in the range of 0.324 to 0.491 V, when the metal centers in the hyperbranched phthalocyanines are changed. It is known that the $V_{\rm OC}$ of DSSCs corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte.^{3,37} However, lower V_{OC} s for cells of 1-5 than those for the cells of N719 were observed. In order to examine the origin of the lower V_{OC} for a monomeric zinc phthalocyanine dye namely PcS6 than for N719, Mori et al. carried out electron lifetimes and densities measurements with various amounts of adsorbed dyes.⁵ In their work, only small difference was observed in the V_{OC}-versus-electron density plot, suggesting a negligible shift of the conduction band edge position among the cells.⁵ Thus, they ascribed the low $V_{\rm OC}$ to the shorter electron lifetime caused by a smaller blocking effect (less compact dye layer).⁵ Similar phenomena have recently been observed in porphyrin-based DSSCs as well.44,45 The smaller blocking effect should also be the reason for the observed low $V_{\rm OC}$ values in the present cases since the relatively large hyperbranched structure of these dyes may make it even more difficult to cover the whole surface of TiO₂. The $V_{\rm OC}$ of the DSSC of 5 was the highest, likely due to the more electron-donating nature of ZnPc which might have provided a more intimate contact with the TiO₂ surface compared to those of other metal centered hyperbranched phthalocyanines. The short circuit current density of the solar cells diverges from a lowest value of 0.425 mA cm^{-2} for the Co counterpart 3 to a highest value of 3.20 mA cm^{-2} for the Zn counterpart 5. Such a remarkable result is probably due to a significantly increased directional electron-transfer property of the zinc phthalocyanine dye by the electron-pushing zinc metal center, and the severely decreased directional electrontransfer property of the cobalt phthalocyanine dye by the

electron-withdrawing cobalt metal center, as compared to the hyperbranched metal-free phthalocyanine $1.^5$ The J_{SC} s of all the solar cells including those for 5 are generally low. This is eventually limited by the narrow absorption of these hyperbranched phthalocyanines.

The photovoltaic performances of 1-5 as discussed above are consistent with the observations from both the steady-state and femtosecond time-resolved fluorescence studies. In particular, the time-resolved fluorescence results have provided information to correlate with the photovoltaic performances of these materials. First, the femtosecond timeresolved fluorescence results provided an insight into the energy flowing after photoexcitation. It has been demonstrated that the excitons are delocalized in the non-aggregated structure of 1, 2, and 5 by their ultrafast depolarization behaviors (Fig. 5).^{17,35} The excitation with each ring seems to have the same energy delocalization feature. For the three materials, after Soret band excitation, energy can transfer fluently from the Soret band to the Q band, and their Q band fluorescences are strong and long-lived, indicating a long lifetime of the excitons. This is usually a prerequisite for an efficient charge separation/injection. While for 3 and 4, the weak or no steady-state Q band emission and/or the ultrafast ISC process restrained the efficiency of electron injection in the devices. The ultrafast ISC process is highly competitive to electron injection. Our previous study revealed that the lowlying triplet-states of CuPc can hardly be harvested by TiO₂ due to the energy level mismatch.¹¹ Since the triplet-states, which hold a dominant share of the excitons, could not be effectively harvested, the $J_{SC}s$ and thus the overall power conversion efficiencies of the DSSCs sensitized by 3 would be low. For 4, after photoexcitation, the energy is more localized around the metal center and likely induces metal-to-ligand charge transfer, resulting in inefficient electron injection. This should be the reason for the worst photovoltaic performance in DSSCs. Besides, the photo-oxidation of Co²⁺ to Co³⁺ might also have dissipated the energy of the primary photoproducts (charges). Second, ultrafast and efficient electron injection processes have been demonstrated at the interface of 5/TiO₂ by femtosecond time-resolved fluorescence study, from which a high IPCE value of the devices of 5 can be anticipated prior to the device fabrication and testing.

Fig. 9(b) shows the IPCEs of the DSSCs of 1–5 with the comprehensive cell structure. The IPCE data are consistent with the results from the absorption spectra as well as the J-V characteristics. The sharpness of the IPCE peaks further confirmed the non-aggregating nature of the phthalocyanine rings on the TiO₂ surface for 2, 3, and 5.⁹ With HBZnPc–COOH (5), the IPCE at the maximum absorption of the Q band reached the highest value of 66.7%. This is consistent with the observation of efficient and ultrafast multi-phasic electron injection at the 5/TiO₂ interface from the femtosecond time-resolved fluorescence studies. Further significant improvement of the performance of the DSSCs based on hyper-branched zinc phthalocyanines is possible, however, *via* structure modification to broaden the spectral response range.

Conclusions

A series of nanostructured non-aggregated hyperbranched phthalocyanines (1-5) have been synthesized, characterized, and applied as TiO₂ sensitizers into red to NIR photon harvestable semi-opaque DSSCs with efficiencies of up to 1.15%. The photovoltaic properties of these materials have been significantly affected by the metal centers. The changing of the metal centers shifted the absorption peaks, resulting in slightly different harvesting capabilities of the solar cells at different wavelengths. The metal centers have changed the HOMO/LUMO energy levels and affected the energy transfer processes within the phthalocyanines, which induced dramatic differences in their photovoltaic performances in DSSCs. The effects of the metal centers have also been observed in porphyrin-based DSSCs.⁴⁶⁻⁴⁸ Zinc was found to be the best metal center in the whole series for designing new hyperbranched phthalocyanine-based DSSCs.

Notably, this work developed a facile avenue of utilizing hyperbranched structure to solve the aggregation issue of phthalocyanine-based dyes on TiO_2 surface which has hindered them from high photovoltaic performances in DSSCs. Ultrafast and efficient multi-phasic electron injection from both the Soret band and *Q* band of 5 to the conduction band of TiO_2 was demonstrated. DSSCs with higher power conversion efficiency are anticipated by broadening the spectral response range of hyperbranched zinc phthalocyanine-based dyes in the visible region through chemical structure modification.

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