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Synthesis, electrochemical, and photophysical studies of hexadecachlorinatedphthalocyaninato zinc(II)

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ABSTRACT

Synthesis of a new symmetrical 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5-dichlorophenyl)phthalocyaninato zinc(II), ZnPc, has been described and characterized by ¹H NMR, ¹³C NMR, MS, UV–Vis, and IR spectrometry. The newly prepared ZnPc is soluble in organic solvents and is not aggregated in solution. The photophysical properties were studied by steady-state absorption and emission, cyclic voltammetry, and nanosecond transient absorption techniques. The prepared ZnPc absorbs and emits at longer wavelengths compared to that of reported phthalocyanine derivatives. The electron-donating properties of the ZnPc have been examined by mixing it with the electron-accepting dicyanoperylene-3,4,9,10-bis(dicarboximide), PDICN₂. The recorded nanosecond transient spectra in the visible/near-IR region showed clearly the electron-transfer from the triplet-excited state of the ZnPc to PDICN₂ with a rate of 3.40×10^8 M⁻¹ s⁻¹. Light absorption in a wide section of the solar spectrum, favorable redox properties, and the electron-transfer properties suggest usefulness of the ZnPc in lightenergy harvesting and developing optoelectronic devices.

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1. Introduction

Phthalocyanines (Pc) have demonstrated several interesting properties such as high chemical and thermal stability, rich redox chemistry, delocalized 18 π -electron system suitable for electron-transfer processes, ability to form complexes with various metal ions, and semi-conducting properties when appropriately self-assembled via π – π stacking interactions [1,2]. These unique properties render them suitable for a number of industrial and medical applications, namely, nonlinear optical devices, electroluminescent displays, photovoltaic cells, low-dimensional conductors, chemical sensors, photodynamic therapy, catalytic activity and biomimetic model systems of the primary processes of natural photosynthesis [3–10].

The properties of phthalocyanines have often been modulated by means of peripheral substituents or axial coordination to the metal center [11–18]. Non-substituted phthalocyanines are sparingly soluble in most organic solvents, hence limiting their

* Corresponding author. Tel.: +966507738708; fax: +96648454770. ** Corresponding author. applications. However, the solubility of Pcs can be improved by introducing different solubility-enhancing substituents such as alkyl, alkoxy, phenoxy and macrocyclic groups and/or a central metal [19]. These substituents enhance the solubility of phthalocyanines and modify their aggregation in solution and other physical properties [20]. Recently, we reported that zinc phthalocyanine derivatives functionalized with substituents such as phenoxy and alkyloxy groups in the peripheral and non-peripheral positions on the benzenoid rings were moderately soluble in common organic solvents. The compounds are potential photosensitizers [21,22] and increased interest has been shown in the synthesis of hexadecasubstituted metal phthalocyanines [22–25].

As a continuation of our ongoing project, we report herein the synthesis of hexadecasubstituted phthalocyaninato zinc(II)(ZnPc) by the substitution of phthalocyanine with hexyloxy groups in non-peripheral positions and chlorinated phenyl groups in peripheral positions, ZnPc **5** (Scheme 1). The presence of bulky substituents in non-peripheral positions leads to a distorted Pc conformation [26,27] with a concomitant modification of the Q-band [28,29]. In this paper, we report the photophysical behaviour of ZnPc **5** and compare the results with the planar zinc tetra-*tert*-butylphthalocyanine, ZnTBPc, (Fig. S1 in the Supporting Information). The electron-transfer (ET) process in a combination of ZnPc **5** with the electron-accepting

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Scheme 1. Synthesis of ZnPc 5.

dicyanoperylene-3,4,9,10-bis(dicarboximide), PDICN₂, has been examined and compared with ZnTBPc/PDICN₂ system to reveal the effect of ring conformation of ZnPc on the rates of the forward electron-transfer and back electron-transfer processes. The reason for choosing such combination of ZnPc/PDICN₂ is that: (1) the combination of the ZnPc/PDICN₂ affords broad absorption bands which can cover about half the useful solar light spectrum, and (2) the phthalocyanine/perylenediimide systems have unique morphology in dispersed heterojunction devices; therefore, both photocurrent generation and charge transport usually function well [30–32] Although there have been several examples of phthalocyanine/perylenediimide ensembles in the literature [33–37], studies of the bimolecular ET process of the phthalocyanine/perylenediimide blends are rare [38] in the literature.

2. Experimental

2.1. General

Dicyanoperylene-3,4,9,10-bis(dicarboximide) were prepared according to the literature [39]. Zinc tetra-*tert*-butylph-thalocyanine (ZnTBPc, 99%) was purchased from Aldrich. All solvents were of analytical grade and were used without further

purification unless otherwise stated. IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrometer FTIR-400 using KBr disks. ¹H NMR spectra were recorded on a Bruker AVANCE 400 MHz and were obtained using the deuterated solvents specified. Microanalyses were performed using a Vario Elemental analyzer CHNS.

Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated benzonitrile (PhCN) containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆; 0.10 M) as supporting electrolyte at 298 K. A conventional threeelectrode cell was used with platinum working electrode (surface area 0.3 mm²) and a platinum wire as counter electrode. The Pt working electrode was polished after each run with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded versus Ag/AgNO₃ reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of argon.

Fluorescence lifetimes were measured by a Photon Technology International model GL-3300 nitrogen laser with a Photon Technology International model GL-302 dye laser, equipped with a fourchannel digital delay/pulse generator (Stanford Research System Inc. DG535) and a motor driver (Photon Technology International MD-5020).

Steady-state absorption spectra were recorded on a Shimadzu UV-3100 PC spectrometer or a Hewlett Packard 8453 diode array spectrophotometer at room temperature. Fluorescence measurements were carried out on a Shimadzu RF-5300PC spectrofluorophotometer. Phosphorescence spectra were obtained by an SPEX fluorolog τ 3-spectrophotometer. For nanosecond transient absorption measurements, deaerated solutions of the compounds were excited by a Panther OPO equipped with a Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) with a power of 10–15 mJ per pulse. The photochemical reactions were monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier Hamamatsu 2949 tube as a detector. Solutions were deoxygenated by argon purging for 15 min prior to the measurements. For the ¹O₂ phosphorescence measurement, an O₂-saturated benzonitrile solution containing the ZnPc sample in a quartz cell (optical path length 10 mm) was excited at 355 nm using a Cosmo System LVU-200S spectrometer. A photomultiplier (Hamamatsu Photonics, R5509-72) was used to detect emission in the near infrared region (band path 1 mm).

2.2. Synthesis of 4,5-dibromo-3.6-dihydroxyphthalonitrile, (1)

To a stirred solution of 3,6-dihydroxyphthalonitrile (5 g, 31.25 mmol) in *tert*-butanol (30 mL) at 45 °C was added *N*-bromosuccinimide, NBS (10.5 g, 64.5 mmol) portion-wise over 25 min. Stirring was continued for 2 h and then more NBS (10.5 g, 64.5 mmol) was added over 25 min. After a further 2 h, the reaction mixture was cooled to room temperature and poured into an aqueous solution of sodium metabisulfite (10 g in 60 mL, excess) at 0 °C with vigorous stirring. The mixture was stirred for 10 min and the precipitate was filtered and washed with cold water (50 mL). The product was dried under vacuum at 60 °C for 24 h to yield 4,5-dibromo-3.6-dihydroxyphthalonitrile as off-white powder (7.8 g, 79%), m.p. 248 °C, IR (KBr): v_{max} cm⁻¹ 2251, 3288 (br).

2.3. Synthesis of 4,5-dibromo-3.6-dihexyloxyphthalonitrile, (2)

A mixture of 4,5-dibromo-3.6-dihydroxyphthalonitrile 1 (2.50 g, 7.86 mmol), triphenylphosphine (4.95 g, 18.9 mmol), and hexanol (1.5 g, 14.7 mmol) was dissolved in dry tetrahydrofuran (80 mL) and cooled to 0 °C. A solution of diisopropyl azodicarboxylate (4.35 g, 21.5 mmol) in tetrahydrofuran (30 mL) was added drop-wise over 30 min. The solution was slowly warmed to room temperature and stirred for an additional 10 h. The solvent was then removed under reduced pressure to give a dark oil, which was dissolved in diethyl ether (20 mL). The solution was filtered to remove undissolved triphenylphosphine oxide. The solvent was evaporated and the remaining residue was purified by column chromatography (silica gel. eluent: *n*-hexane/tetrahydrofuran 10:1). The product was recrystallized from cyclohexane to obtain 4.5-dibromo-3.6-dihexyloxyphthalonitrile. Yield (2.72 g, 76%) as white powder. m.p. 39-41 °C. C₂₀H₂₆Br₂N₂O₂: C, 49.4; H, 5.39; N, 5.76%. Found: C, 50; H, 5.56; N, 5.95. ¹H NMR (400 MHz, CDCl₃): 0.91 (6H, t), 1.33–1.38 (8H, m), 1.48–1.56 (4H, m), 1.86–1.93 (4H, m), 4.2 (4H, t) ppm. ¹³C NMR (400 MHz, CDCl₃): 13.98, 22.5, 25.29, 29.92, 31.43, 109.21, 112.36, 129.6, 156.39 ppm.

2.4. Synthesis of 4,5-bis(3.5-dichlorophenyl)-3,6-bis(hexyloxy) phthalonitrile, (**4**)

4,5-bis(3.5-dichlorophenyl)-3,6-bis(hexyloxy)phthalonitrile **4** was prepared from 3,5-dichlorophenylboronic acid **3** (260 mg, 1.64 mmol). Purification of the product was achieved by column chromatography (silica gel, eluent: petroleum ether/ethyl acetate 100:2.5 v/v). 37% yield (101 mg) as white powder. m.p. 190 °C. IR

(KBr): $\nu_{max} \text{ cm}^{-1} 806$, 1176 (C–O–C), 1303, 1369, 1465, 1589 (C=C), 2233 (C=N), 1562, 2869, 2931, C₃₂H₃₂Cl₄N₂O₂: C, 62.15; H, 5.22; N, 4.53%. Found: C, 62.1; H, 5.3; N, 4.53. ¹H NMR (400 MHz, CDCl₃): 0.84 (6H, t, 2CH₃), 1.09–1.26 (12, m, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.5–1.55 (4H, quin, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.8 (4H, t, OCH₂), 6.9 (4H, s, Ar–H), 7.31 (2H, t, Ar–H). ¹³C NMR (400 MHz, CDCl₃): 13.97 (CH₃), 22.46 (CH₂), 25.26 (CH₂), 29.73 (CH₂), 31.30 (CH₂), 76.35 (OCH₂), 112.48 (C), 128.73 (2 × CH), 128.45 (CH), 132.24 (C), 134.99 (C), 135.63 (C), 139.57 (C–Cl), 156.17 (CN) ppm.

2.5. Synthesis of 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16,17,23,24-octa-(3,5-dichlorophenyl)phthalocyaninato zinc(II), (ZnPc 5)

A mixture of **4**, zinc acetate dihydrate (25 mg, 0.11 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-pentanol (5 mL) was heated at reflux for 24 h with stirring under nitrogen. The reaction mixture was cooled to room temperature and the solvent was rotary evaporated under reduced pressure to obtain a green deposit, which was dissolved in methanol (5 mL) and the solution was filtered to remove the solid impurities. The solvent was rotary evaporated under reduced pressure and the remaining residue was purified by column chromatography (silica gel, eluent: n-hexane/ethyl acetate 10:0.2 mL). Complex 5 was precipitated from methanol as green powder. Yield (6.8 mg, 15%). IR (KBr): *v*_{max} cm⁻¹ 804, 1170 (C–Cl), 2862, 2928 (CH₂), 2951 (Ar–CH). C₁₂₈H₁₃₀Cl₁₆N₈O₈Zn: C, 60.5; H, 5.16; N, 4.41%. Found: C, 60.96; H, 5.69: N. 4.11. MALDI-MS: isotopic cluster at 2540 [M⁺]. ¹H NMR (400 MHz, CDCl₃): 0.88 (24H, t, 8 -CH₃), 1.12-1.29 (64H, m), 4.75 (16H, br, 8 OCH₂), 7.34 (16H, br, Ar–H), 7.37 (8H, t, Ar–H). ¹³C NMR (400 MHz, CDCl₃): 14.2 (CH₃), 22.3 (CH₂), 26.2 (CH₂), 30.20 (CH₂), 32.0 (CH₂), 77.1 (OCH₂), 127.1 (2 CH), 130.1 (CH), 130.9 (C), 134.2 (C), 136.1 (C), 139.6 (C), 150.8 (C), 152.2 (C) ppm.

3. Results and discussion

3.1. Synthesis

Compound 4,5-dibromo-3.6-dihydroxyphthalonitrile **1** was synthesized according to published procedure [40]. There are two bromine substituents and two phenolic groups that can be used to introduce two different substituents at the 3.6- and 4,5-positions of the phthalonitrile. The *Mitsunobu reaction* was utilized to rapidly alkylate the two alcohol groups at low temperature to obtain 4,5-bromo-3,6-dihexyloxyphthalonitrile, **2**. This reaction is used to dehydrate alcohols and phenols using triphenylphosphine and diisopropyl azodicarboxylate (DIAD) [41]. Subsequently, *Suzuki reaction* was applied to introduce the two substituted phenyl groups at the 4- and 5-positions in the phthalonitrile derivative.

Compound 4 was prepared by the reaction of 4,5-dibromo-3,6-dihexyloxyphthalonitrile **2** with 3,5-dichlorodphenylboronic acid **3**, Scheme 1. Compound **4** was purified chromatographically to give 37% yield. The ¹H NMR spectrum showed all the substituents and ring protons in their respective regions. For compound **4** the aromatic region displayed one triplet of triplet at 7.31 ppm and one doublet peak at 6.9 ppm which can be attributed to the six aromatic protons for each compound. IR spectra clearly indicated the formation of compound **4** with the appearance of nitrile stretching frequency at 2233 cm⁻¹.

The target ZnPc **5** presented in Scheme 1 was synthesized by cyclotetramerization of **4** following the phthalocyanine synthetic procedure reported previously [22]. The reaction of phthalonitrile **4** with zinc acetate dihydrate in DBU under reflux for 24 h afforded **5** in 15% yield.

The structure of ZnPc **5** was elucidated by spectroscopic and analytical tools. For example, the IR spectrum showed the disappearance of the sharp C \equiv N stretching frequency at 2233 cm⁻¹, consistent with the cyclotetramerization of **4**. ¹H NMR spectrum of **5** showed one triplet signal at 7.37 ppm attributed to the 8 CH-aromatic protons, and one broad signal at 7.34 ppm attributed to another 16 aromatic protons. The triplet at 0.88 ppm integrated for 24 protons assigned to the terminal methyl groups. The 16 meth-yleneoxy proton resonances at 4.75 ppm appear as broad signal. Further elucidation of **5** was proved by mass spectrometry, which showed a molecular ion-peak at 2540 *m/e*.

3.2. Steady-state absorption and emission studies

As shown in Fig. 1, the toluene solution of ZnPc shows absorption around 361 nm attributed to the phthalocyanine Soret band, whereas the strong absorption at 748 nm with two vibronic shoulders at 668 and 713 nm was attributed to phthalocyanine Q-bands that arise from $\pi - \pi^*$ transitions. The weak absorption around 410 nm is common in alkoxy-substituted phthlalocyanines, which is attributed to $n-\pi^*$ transitions [42,43]. On the other hand, the absorption spectrum of the extensively studied ZnTBPc exhibited absorptions of the Soret and Q-bands at 347 and 677 nm, respectively. From this comparison, the Q-band of the examined ZnPc 5 exhibit red shift by approximately 82 nm compared to that of the reference ZnTBPc. The red shift of the absorption ZnPc **5** can be rationalized by the higher conjugation of ZnPc 5. It is worth mentioning that the observed shift is consistent with the trend detected upon distortion from planarity of the 18 π -electron system of porphyrins [44], taking into account that the presence of bulky substituents in non-peripheral positions leads to a distorted Pc conformation [26,27] with a concomitant modification of the O-band [28.29]. It was found that addition of ferric perchlorate to a benzonitrile solution containing ZnPc **5** resulted in a remarkable spectral change in the range of 800-1000 nm. The radical cation of ZnPc (ZnPc⁺) was clearly observed at 810 nm, which is blue-shifted by approximately 40 nm compared to that of the ZnTBPc radical cation (ZnTBPc++) (Fig. S3 in the Supporting Information).

Steady-state fluorescence spectroscopy was used to probe the excited state properties. Upon 640 nm light excitation, the fluorescence emission spectrum of ZnPc exhibited a band at 753 nm (Fig. 1, right) which was red-shifted by approximately 59 nm compared with ZnTBPc. The fluorescence lifetime of the single-t-excited state of ZnPc exhibited mono-exponential decay with a lifetime ~2.50 ns (Fig. S4), which is slightly shorter compared with ZnTBPc [45].



Fig. 2. Transient absorption spectra of ZnPc (0.1 mM) by nanosecond-laser excitation in deaerated benzonitrile; $\lambda_{ex}=430$ nm. Inset: Time profile at 630 nm.

3.3. Photoinduced electron-transfer reaction of ZnPc ${\bf 5}$ with PDICN_2 in benzonitrile

Upon photoexcitation of ZnPc in deaerated benzonitrile, the nanosecond transient spectrum of ZnPc **5** at 3 μ s exhibited absorption in the range of 400–850 nm with a maximum at 630 nm (Fig. 2), which corresponds to the triplet-excited state of ZnPc (³ZnPc^{*}). The ³ZnPc^{*} decayed within 200 μ s with a rate constant 1.7 × 10⁴ s⁻¹, from which the lifetime of the ³ZnPc^{*} was found be as 59 μ s. The absorption band of the ³ZnPc^{*} exhibited a red shift by approximately 140 nm compared to that of the triplet-excited state of ZnTBPc [24].

To examine the electron-donating effect of ZnPc, the nanosecond transient spectra were recorded for a mixture of ZnPc with the electron-acceptor PDICN₂ in benzonitrile (Fig. 3 and Figs. S5 and S6). Photoexcitation of ZnPc (0.05 mM) in the presence of PDICN₂ (0.00–0.08 mM) by a 430 nm laser source resulted in the characteristic absorption band of the triplet-excited of ZnPc (³ZnPc*) at 630 nm. With the decay of the triplet-excited state of ZnPc, there was a concomitant rise of the characteristic absorption band of the PDICN₂ radical anion (PDICN₂•⁻) in the visible-near-IR region with maxima 694, 773, and 935 nm [46,47]. The absorption band of PDICN₂⁻⁻ was confirmed by treating PDICN₂ with tetrakis(dimethylamino)ethylene (TDAE) in benzonitrile (Fig. S7 in the Supporting Information). In addition, the absorption band of



Fig. 1. Steady-state absorption spectra of ZnPc 5 and ZnTBPc in benzonitrile. (Right) Steady-state fluorescence spectra of ZnPc 5 and ZnTBPc in benzonitrile; $\lambda_{ex} = 640$ nm.



Fig. 3. (Left) Nanosecond transient spectra of ZnPc (0.05 mM) in the presence of PDICN₂ (0.08 mM) in deaerated benzonitrile, $\lambda_{ex} = 430$ nm. Inset: Rise-profile of PDCN₂ - at 940 nm (Right) Dependence of the decay-rates of the ³ZnPc^{*} at 630 nm on concentration of PDICN₂ in benzonitrile. Inset: Pseudo first-order plot.

the ZnPc radical cation (ZnPc^{•+}) was clearly observed at 810 nm. The decay of ³ZnPc^{*} and the rise of ZnPc^{•+}/PDICN₂•⁻ seem to match, which provides evidence for electron-transfer via ³ZnPc^{*}. This was supported by bubbling oxygen into the solutions where an intermolecular energy-transfer from the ³ZnPc^{*} to oxygen emerged, suppressing the electron-transfer process. These processes are summarized in Scheme 2. The electron-transfer from the tripletexcited stat of ZnPc to PDICN₂ in polar benzonitrile solvent can be rationalized as follows: polar solvent molecules rapidly surround the radical ions once formed and consequently prevent the electron return. The escape from the solvent cage is indeed a key feature of electron-transfer in solution [48,49].

More details on the kinetics of the electron-transfer process are shown in Fig. 3, where the rate constant of the electron-transfer process (k_{et}) was evaluated by monitoring the decay of ³ZnPc^{*} and the rise of PDICN₂-⁻ as a function of PDICN₂ concentration. The decay profiles of ³ZnPc^{*} obeyed first-order kinetics; each rate constant is referred to (k_{1st}). The linear concentration-dependence of the observed k_{1st} values gives the k_{et} value, calculated as 3.40×10^8 M⁻¹ s⁻¹. This k_{et} value is much smaller compared with



Scheme 2. Electron-transfer process of ZnPc/PDICN2 system in benzonitrile.

the diffusion-control limit (k_{diff}) in benzonitrile [50]. The smaller k_{et} value of ZnPc/PDICN₂ system is actually due to the steric hindrance of the electron donors in ZnPc.

The electron-transfer process via the triplet-excited state of ZnPc was supported from the viewpoint of thermodynamics of electron-transfer process. The electrochemical measurements were carried out using CV and DPV techniques at a glassy carbon electrode in a solution of carefully dried benzonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆; 0.1 M) at room temperature (Fig. 4). The measurements show the oxidation potentials (E_{ox}) of the ZnPc at 0.41 and 0.81 V vs Ag/AgNO₃, which comparable to that of ZnTBPc. On the other hand, the reduction potentials (E_{red}) of PDICN₂ were located at -0.58 and -0.98 V vs Ag/ AgNO₃ (Fig. S8 in the Supporting Information). Based on the first E_{ox} of ZnPc, the first E_{ox} of PDICN₂, and the triplet energy of ZnPc, the free-energy change of the electron-transfer process $(-\Delta G_{et}^T)$ via the triplet-excited state of ZnPc was estimated as 0.30 eV, corresponding to 28.09 kJ mol⁻¹ [51,52]. The negative $-\Delta G_{et}^{T}$ value *via* the triplet-excited state of ZnPc suggests that the quenching process is close to the diffusion-controlled limit (k_{diff}).

In the long time-scale (2 ms), PDICN₂•⁻ radical anion begins to decay slowly after reaching the maximal absorbance (Fig. 5). The decay time profile was fitted with second-order kinetics, suggesting that bimolecular backward electron-transfer process between ZnPc•⁺ and PDICN₂•⁻ takes place. The rate constant of backward electron-transfer (k_{bet}) between ZnPc•⁺ and PDICN₂•⁻ was estimated at $1.03 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from the slope of the second-order plot in the form of k_{bet}/ε , where ε is the molar extinction coefficient of PDICN₂•⁻ ($\varepsilon = 1.81 \times 10^4$) [50]. The obtained k_{bet} for ZnPc•⁺ and PDICN₂•⁻ is smaller than the diffusion-control limit in benzonitrile [50].

In the case of the ZnTBPc/PDICN₂ mixture system, the electrontransfer process from the triplet-excited state of ZnTBPc to the PDICN₂ was confirmed by recording the absorption bands of the radical ions (Figs. S9–S12 in Supporting Information). The k_{et} and



Fig. 4. CV (left) and DPV (right) of ZnPc 5 in deaerated benzonitrile. Sweep rate: 50 mV s⁻¹.



Fig. 5. Decay of $ZnPc^+/PDICN_2^{--}$ on long time-scale produced under the same conditions as described in Fig. 3. Inset: Second-order plot.

 $k_{\rm bet}$ values were found to be 1.26×10^9 M⁻¹ s⁻¹ and 1.71×10^9 M⁻¹ s⁻¹, respectively. The finding that the value of $k_{\rm bet}$ of ZnPc/PDICN₂ is smaller than that of ZnTBPc/PDICN₂ reflects the effect of the bulky substituents of ZnPc in slowing the rate of ET via the triplet-excited state. The steric effect probably decreases the solvation of the radical ion in the pair because of shielding of the polar solvent molecules, thus decreasing the $k_{\rm bet}$ value of ZnPc/PDICN₂ system.

4. Conclusion

The present work describes the synthesis and characterization of a new symmetrical 1,4,8,11,15,18,22,25-octahexyloxy-2,3,9,10,16, 17,23,24-octa-(3,5-dichlorophenyl)phthalocyaninato zinc(II). The synthesized complex possessed high solubility in various organic solvents such as CH₂Cl₂, THF, acetone and ethyl acetate. The presumably distorted ZnPc absorbed and emitted at longer wavelengths compared with the planar ZnTBPc. The bimolecular electron-transfer in ZnPc/PDICN2 system was confirmed by observing the transient absorption spectra of $ZnPc^{+}$ and $PDICN_2^{-}$ in the visible and near-IR region. The observed k_{bet} of the ZnPc++/PDICN2+was found to be considerably smaller than that of ZnTBPc+/ PDICN₂•⁻ reflecting the effect of the bulky groups in slowing the electron-transfer in ZnPc/PDICN₂ system. The absorption in a wide section of the solar spectrum, favorable redox properties, and the electron-transfer properties suggest the usefulness of the ZnPc in light energy-harvesting and developing optoelectronic devices.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2011.03.028.

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