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Tetrahedron Letters 45 (2004) 7617–7620

Tetrahedron Letters

Light-harvesting composites of directly connected porphyrin–phthalocyanine dyads and their coordination dimers

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Received 6 July 2004; revised 11 August 2004; accepted 18 August 2004

Abstract—Directly linked porphyrin (**Por**)–phthalocyanine (**Pc**) heterodyads (**H_2Por–H_2Pc** and **H_2Por–ZnPc**) with an imidazolyl group at porphyrin's *meso*-position were synthesized. Introduction of a zinc ion into the porphyrin afforded stable complementary dimers of the heterodyads. The heterodyads and their dimers gave extensive and strong absorption bands owing to the porphyrin and phthalocyanine components and induced an efficient energy transfer from porphyrin to phthalocyanine. Strong fluorescence from phthalocyanine was observed in the case of **H_2Por–H_2Pc**.

Sunlight contains a continuous spectrum of wavelengths in the visible region of 400–800 nm. Use of the broadest possible range of the visible spectrum is important to ensure maximum use of solar energy. Organic materials that absorb various wavelengths of visible light and fluorescence with high efficiency are good candidates for organic photoelectronic devices, such as photosensitizing solar cells[1] and organic light emitting diodes.[2] Porphyrins have frequently been used in such devices[3] because of their excellent photochemical properties, in particular, a very strong absorption band around 410 nm (Soret band) and medium-strength bands in the range of 510–650 nm (Q-bands). Phthalocyanines have found even more diverse applications;[4] their strong absorption bands occur around 350 nm (Soret band) and in the range of 600–700 nm (Q-bands). Fluorescence quantum yields of phthalocyanines (typically 650–850 nm, $\Phi_F = 0.77$ for *t*-Bu_4Pc)[5] are generally much larger than those of porphyrins (typically 600–700 nm, $\Phi_F = 0.11$ for TPP).[6] Since the absorption wavelength of phthalocyanine mostly overlaps with the fluorescence wavelength of porphyrin, an efficient energy transfer is expected from porphyrin to phthalocyanine. Thus, composites containing porphyrin and phthalocyanine in the same molecular framework are expected to be effective in capturing a wide range of visible light and emitting red light efficiently. Porphyrin–phthalocyanine heterodyads linked through various spacers, such as ether,[7] alkoxy,[8] piperazinyl,[9] phenylethynyl,[10–13] and ethynyl groups,[14] have been reported in the past. Among these, only ethynyl-linked heterodyad of porphyrin and phthalocyanine showed the absorption spectrum different from the sum of those of two components, thus expanding effectively the absorption range by conjugation. However, fluorescence from the phthalocyanine part was almost completely quenched. On the other hand, intense fluorescence was reported only for the phenylethynyl-linked dyad. In turn, the absorption spectrum was the sum of those of two components without the effect to cover a wider range of the absorption wavelength by the link.

Another strategy to expand the range of absorption wavelength maintaining strong fluorescence is to use the excitonic coupling between chromophores. The strategy is widely employed in natural light-harvesting systems, most typically in photosynthetic bacteria,[15,16] and introduced into synthetic multi-porphyrin systems linking by direct *meso–meso* connections[17] or through phenylene[18] or naphthalene groups,[19] or coordination organization of imidazolyl-[20] or pyridyl-appended[21] porphyrinatozinc. The degree of excitonic coupling and energy transfer depends strongly on mutual orientation and distance of chromophores.

In this letter we report the first synthesis of porphyrin (**Por**)–phthalocyanine (**Pc**) heterodyads **H_2Por–H_2Pc (3H_2)**, and **H_2Por–ZnPc** (**3Zn**) connected directly

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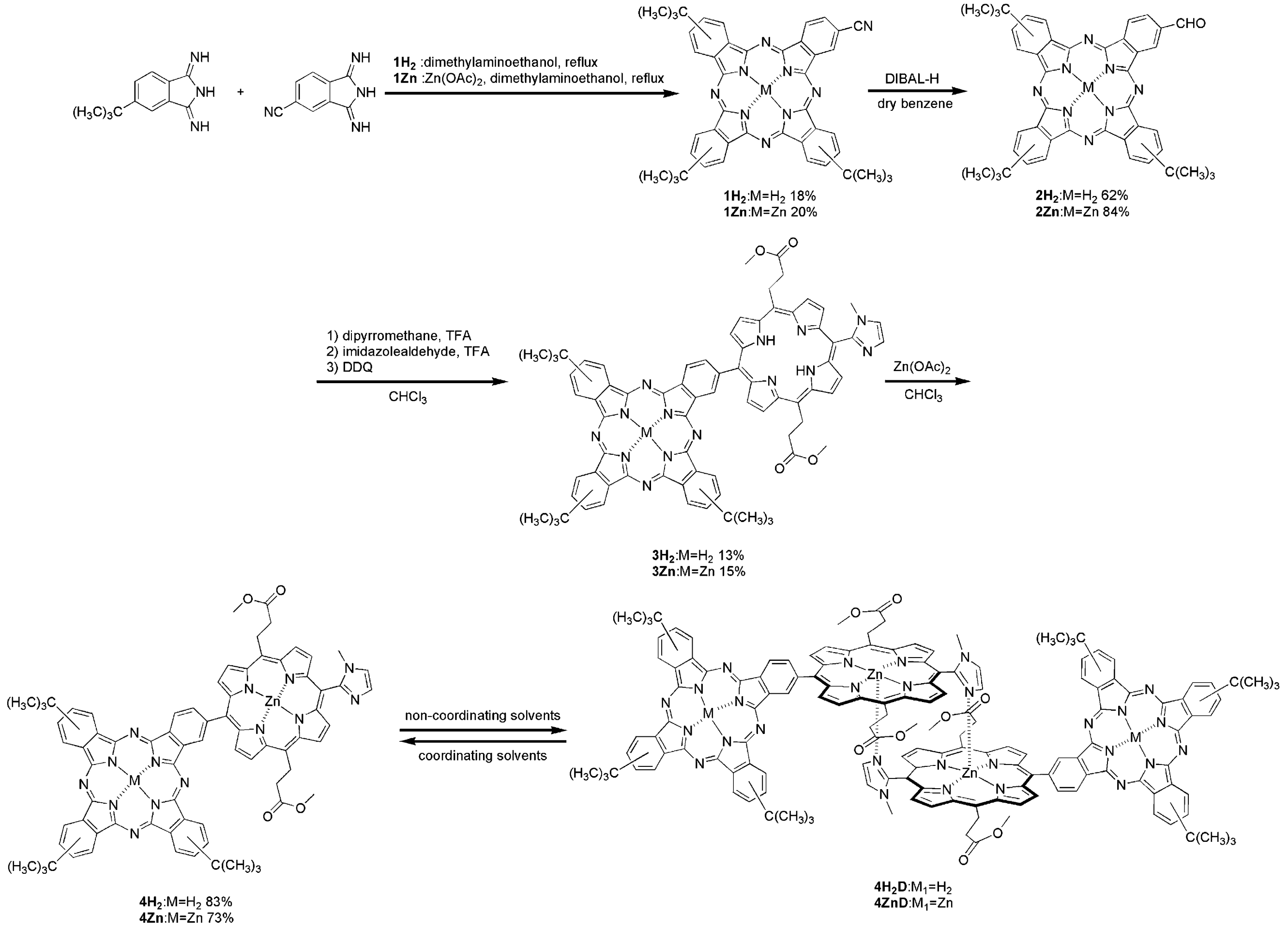
doi:10.1016/j.tetlet.2004.08.101

at *meso*- and β-positions of porphyrin and phthalocyanine, respectively. Edge-to-edge distance between porphyrin and phthalocyanine is estimated to be 1.5 Å, the closest in the series of heterodyads,[7–14] which is expected to result in strong excitonic coupling. Furthermore, the two chromophores are of orthogonal geometry, and intermolecular π–π stacking of porphyrin and phthalocyanine can safely be avoided. In addition, the imidazolyl substituent afforded a scaffold of stable coordination dimers to give rise to the formation of dimers of porphyrin–phthalocyanine dyads [**ZnPor–$\mathbf{H_2}$Pc**]$_2$ (**4$\mathbf{H_2}$D**) and [**ZnPor–ZnPc**]$_2$ (**4ZnD**). Dyad **3$\mathbf{H_2}$** was synthesized as illustrated in Scheme 1. Monocyano-substituted phthalocyanine **1$\mathbf{H_2}$** as a mixture of positional isomer was prepared by condensation of 4-cyanodiiminoisoindoline and 4-*tert*-butyldiiminoisoindoline. Reduction of **1$\mathbf{H_2}$** with diisobutylaluminium hydride (DIBAL-H) in benzene gave aldehyde **2$\mathbf{H_2}$** at 62% yield. Condensation of **2$\mathbf{H_2}$** with methoxycarbonylethyldipyrromethane and 1-methylimidazole-2-carboxyaldehyde in the presence of trifluoroacetic acid (TFA) followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded dyad **3$\mathbf{H_2}$** in 13% yield. Zinc phthalocyanine derivative **3Zn** was synthesized similarly from phthalocyaninatozinc **1Zn**, which was prepared by condensation of 4-cyanodiiminoisoindoline and 4-*tert*-butyldiiminoisoindoline in the presence of Zn(OAc)$_2$. Dimers of dyads **4$\mathbf{H_2}$D** and **4ZnD** were obtained by introduction of zinc ions into the porphyrin part of **3$\mathbf{H_2}$** and **3Zn**. These dimers contain positional and rotational isomer. The complementary dimer formation at the porphyrin part was confirmed most strongly by the large split Soret band at around 410 and 440 nm induced by the exciton interaction, and the large higher field shift of coordinating imidazolyl groups. This characteristic structure proof has been extensively developed by us. Identification of **3$\mathbf{H_2}$**, **3Zn**, **4$\mathbf{H_2}$D**, and **4ZnD** were established by ^{1}H NMR, UV–vis spectroscopy, and MALDI-TOF mass spectrometry. Purity of **3$\mathbf{H_2}$** and **3Zn** was determined by analytical GPC.[22]

UV–vis spectra of **3$\mathbf{H_2}$**, **3Zn**, **4$\mathbf{H_2}$D**, and **4ZnD** in toluene are shown in Figure 1. Absorption spectra of an equimolar mixture of the monomers **$\mathbf{H_2}$Pc** (tetra-*tert*-butylphthalocyanine) and **$\mathbf{H_2}$Por** [5-imidazolyl-10,20-bis(methoxycarbonylethyl)-15-phenylporphyrin],[23] and the monomers of zinc complexes, **ZnPc** and **ZnPor**,[24] were superimposed in the corresponding figures for easy comparison. Self-assembled dimerization of **ZnPor** was observed as two split Soret bands[20] at 413 and 437 nm in Figure 1C and D. In all cases, Q-bands of phthalocy-



Scheme 1. Synthetic pathway of dyads (**3$\mathbf{H_2}$** and **3Zn**) and their coordination dimers (**4$\mathbf{H_2}$D** and **4ZnD**).

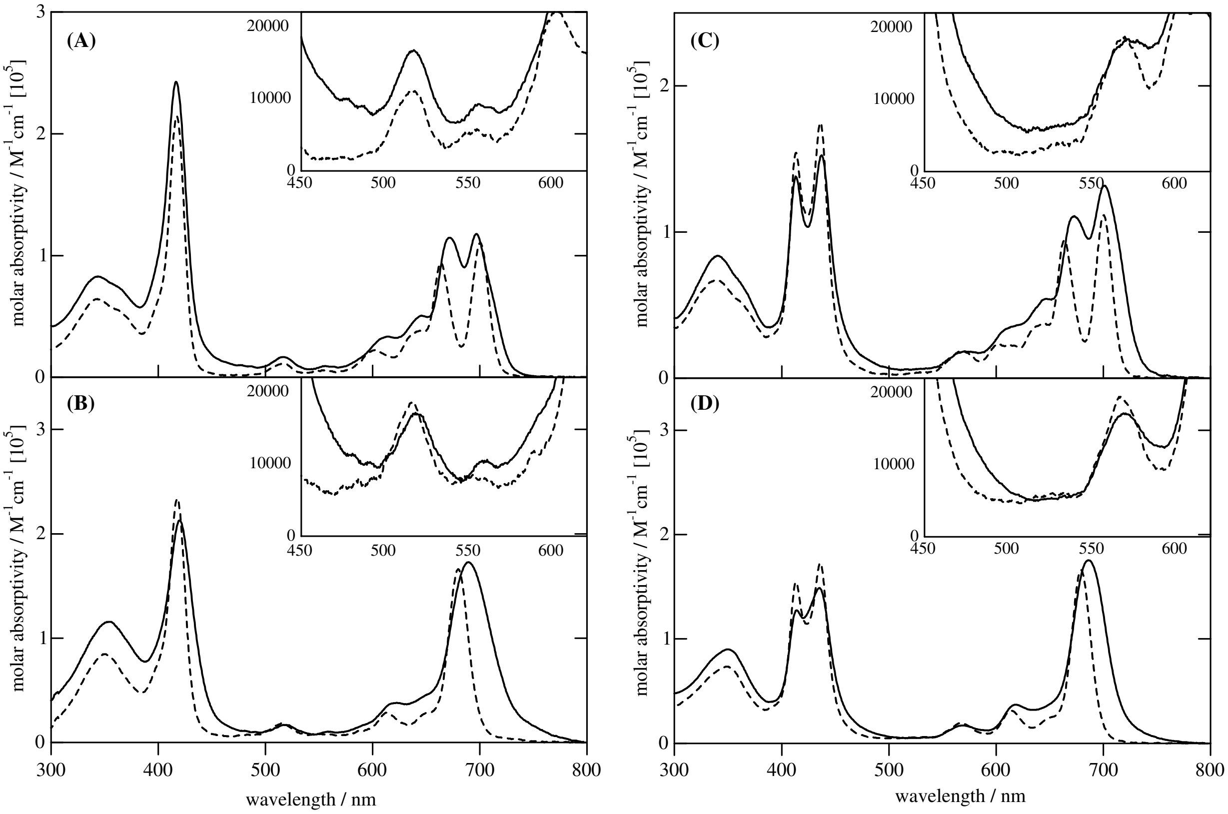


Figure 1. UV–vis spectra of **3H$_2$** (A), **3Zn** (B), **4H$_2$D** (C), **4ZnD** (D) (solid line) and those of an equimolar mixture of the corresponding monomers, **MPc** (**M** = **H$_2$**, **Zn**), and **MPor** (**M** = **H$_2$**, **Zn**) (broken line) in toluene. Inset: Expanded absorption spectra in the range of 450–650nm.

anine moieties broadened significantly and their λ_{max}'s were shifted to longer wavelengths by 7–10nm to allow increased absorption of visible light in the 600–730nm range. The Soret band regions of porphyrin moieties also changed. In the case of dyads **3H$_2$** and **3Zn**, the half-band widths of the Soret bands increased from 17 to 25nm and from 20 to 35nm, respectively. In the case of dimeric dyads **4H$_2$D** and **4ZnD**, the split of the Soret band effectively covers the wavelengths from 400 to 460nm. The extinction coefficients of all the composites were larger than $6\times10^3\,M^{-1}cm^{-1}$ in the whole range of 300–730nm, and especially high (2×10^4–$2\times10^5\,M^{-1}cm^{-1}$) in the 300–450 and 600–730nm range. In order to evaluate the light-harvesting ability of synthesized monomeric and dimeric dyads, fluorescence spectra were measured by excitation at various wavelengths in toluene. In all cases, even selective excitation at the absorption band of the porphyrins (516nm for **3H$_2$** and **3Zn**, 450nm for **4H$_2$D** and **4ZnD**) gave strong fluorescence from the phthalocyanine moieties, indicating that almost perfect energy transfer occurred from porphyrin to phthalocyanine. Figure 2 compares fluorescence spectra of **3H$_2$** and the equimolar mixture of **H$_2$Por** and **H$_2$Pc** by selective excitation of the porphyrin part at 516nm.[25] The emission from the phthalocyanine part in **3H$_2$** was strong, whereas that from the porphyrin part disappeared almost completely. The fluorescence quantum (Φ_F) yield of **3H$_2$** from the phthalocyanine part itself was 0.71.[26] The value is close to that of $\Phi_F = 0.77$ of **H$_2$Pc**,[5] and much larger than $\Phi_F = 0.14$ of the corresponding porphyrin monomer **H$_2$Por**. It is noteworthy that direct connection of porphyrin to phthalocyanine keeps the inherent high fluorescence quantum yield of phthalocyanine. On the other hand, the fluorescence quantum yields of **3Zn**, **4H$_2$D**, and **4ZnD** were decreased considerably, Φ_F being 0.17, 0.20, and 0.12, respectively, compared with those of **H$_2$Pc** and **ZnPc** ($\Phi_F = 0.30$).[27] Since almost no fluorescence was

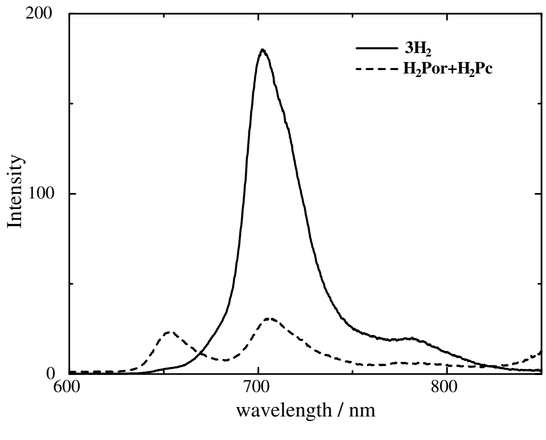


Figure 2. Fluorescence spectra of **3H$_2$** (solid line) and an equimolar mixture of **H$_2$Por** and **H$_2$Pc** (broken line) by selective excitation of the porphyrin part at 516nm.

observed from porphyrin in these cases, electron transfer either to or from phthalocyanine must be taking place in these composites. Electrochemical and transient photophysical properties are interesting in these cases and detailed analyses are now under way.

In conclusion, we synthesized porphyrin–phthalocyanine dyads directly connected at their *meso*- and β-positions, respectively. The dyads and their coordination dimers gave extensive and strong absorption bands owing to the porphyrin and phthalocyanine components and their strong excitonic coupling by closely located chromophores. The extinction coefficients of all the compounds reached 2×10^{4}–$2\times10^{5}\,M^{-1}cm^{-1}$ in the 300–450 and 600–700 nm range. Efficient energy transfer from porphyrin to phthalocyanine and strong fluorescence from the latter were observed for free-base porphyrin–phthalocyanine dyads **$3H_2$**. These properties make the compound an excellent light-harvesting material.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.08.101.

References and notes

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24. **ZnPor** was prepared by treatment of $Zn(OAc)_2$ with **H_2Por**. Spectroscopic data for **ZnPor**: ^1H NMR ($CDCl_3$): δ 9.60 (d, $J = 4.86$ Hz, 2H, β-pyrrole), 9.06 (d, $J = 4.86$ Hz, 2H, β-pyrrole), 8.94 (d, 2H, $J = 4.59$ Hz, β-pyrrole), 8.67 (d, $J = 7.29$ Hz, 2H, Ph), 8.13 (d, $J = 7.56$ Hz, 2H, Ph), 7.90–7.97 (m, 3H, Ph), 7.80 (t, $J = 1.35$ Hz, 1H, Ph), δ 5.53 (d, $J = 1.35$ Hz, 1H, Im CH), 5.48 (br s, 4H, ester β), 5.47 (d, $J = 4.59$ Hz, 2H, β-pyrrole), 3.92 (s, 6H, COOMe), 3.60–3.86 (m, 4H, ester α), 2.13 (d, $J = 1.35$ Hz, 1H, Im CH), 1.67 (s, 3H, NMe); MALDI-TOF MS: *m/z* calcd for $C_{38}H_{32}N_6O_4Zn$ 700.18, found 700.28 (M+).
25. Fluorescence spectra of **3Zn**, **$4H_2D$**, and **4Zn** in comparison with those of equimolar mixture of **MPor** (**M = H_2, Zn**), and **MPc** (**M = H_2, Zn**) are shown in Supplementary data.
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