

The First Two Novel Phthalocyanine-Based Dyads[§]

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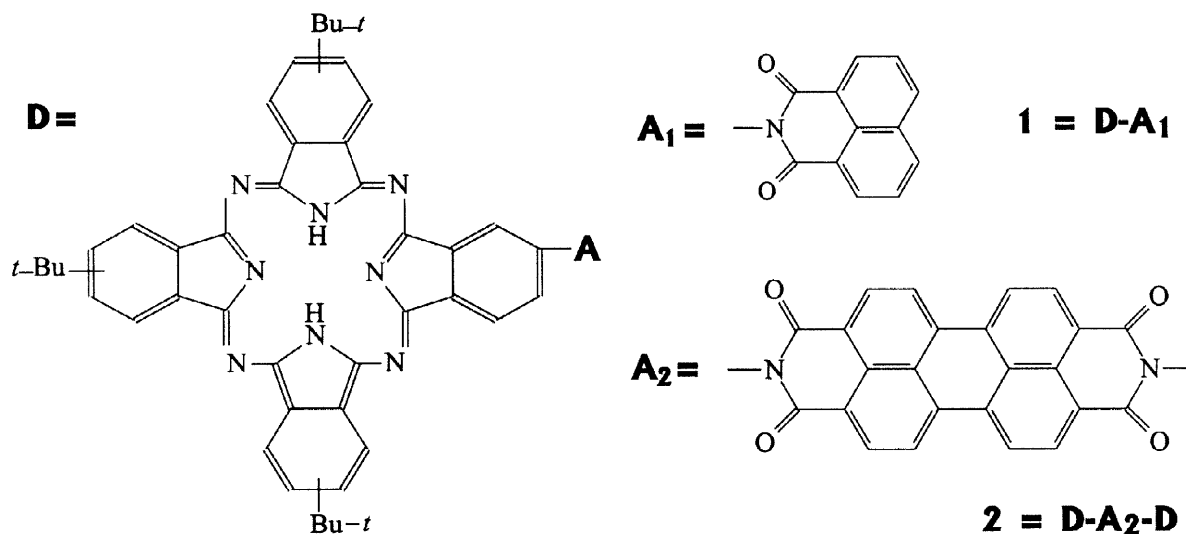
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Abstract. Tri-*tert*-butylphthalocyanine and 1,8-naphthaimide or 3,4,9,10-perylenebis(dicarboximide) have been covalently linked in close proximity *via* a C–N bond. Through-bond electronic interaction between the two chromophores is demonstrated by electronic spectroscopy.

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Phthalocyanines (Pcs) possess a wide range of physical and chemical properties that make them interesting building blocks for supermolecular assemblies and new materials, in which they can exhibit electron donating property.^{1–4} Their covalently linking with suitable electron acceptors may offer some interesting possibilities for electronic interaction and modification.⁵ We report here the first two examples of this effort: 1,8-naphthaimidetri-*tert*-butylphthalocyanine (**1**) and N,N'-di(tri-*tert*-butylphthalocyanine)-3,4,9,10-perylenebis(dicarboximide) (**2**), shown below, both of which have important features of good solubility and demonstrable electronic interaction between the chromophores.



1 and **2** were prepared by the condensation of aminotri-*tert*-butylphthalocyanine (AmBuPc)⁶ and 1,8-naphthalic anhydride or 3,4,9,10-perylenetetracarboxylic dianhydride in quinoline at a high temperature (200–240 °C) under nitrogen in the presence of molecular sieves (4 Å) for 4 h and separated, purified by column chromatography on silica gel (10–40 μm) for at least 4 times eluting with chloroform combined with extracting with methanol for 6 h and drying under vacuum for 12 h at 90 °C.⁷

Both of the compounds **1** and **2** show their parent ion peaks in the FD mass spectra and characteristic C=O stretching vibration absorptions between 1738 and 1618 cm^{-1} together with those of asymmetrically substituted metal-free phthalocyanines in their IR spectra,⁸ such as, the weak absorption band at about 3290 cm^{-1} is observed in the spectra of the two compounds and this could be assigned to the stretching vibration of N—H bond. Peaks at around 1460, 1320 and 1260 cm^{-1} indicate the presence of C—N aromatic stretching. The bands at about 1090, 1010, 910, 890, 830 and 750 cm^{-1} could be assigned to the various phthalocyanine skeletal vibrations, such as the band at about 1010 cm^{-1} is the characteristic band of the metal-free phthalocyanine ring vibration.⁶

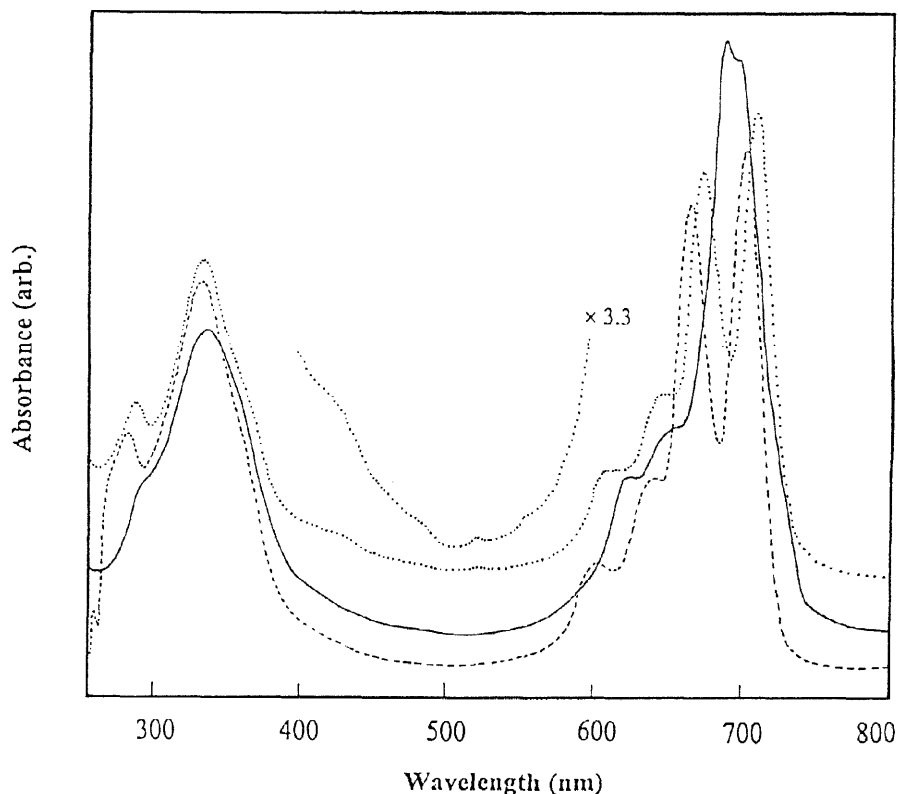


Figure 1. Comparison of the UV-vis spectrum of the compounds **1** (dashed line), **2** (dotted line) with the reference compound AmBuPc (solid line) in chloroform ($[\text{compound}] \approx 10^{-5}$ M). The relative intensity of Q_{max} and B_{max} , *i.e.*, $Q_{\text{max}}/B_{\text{max}}$ values for the compounds **1**, **2** and AmBuPc are about 1.33, 1.50 and 1.87, respectively. It is observable for the weak absorptions at around 480, 520 and 554 nm of 3,4,9,10-perylenebis(dicarboximide) component in the spectrum of **2**, see the enlarged section with dotted line.

The interaction between the two chromophores phthalocyanine and 1,8-naphthaimide or 3,4,9,10-perylenebis(dicarboximide) was examined by electronic absorption and emission spectroscopy. For both of the two compounds, their absorption spectra show the characteristic B and Q bands of phthalocyanines, such as, they show a doublet at around 670 and 700 nm together with two shoulders at around 600 and 640 nm in the Q band region (500–800 nm) and in the B band region (260–500 nm), they show a peak at about 340 nm with a shoulder between 280 and 300 nm. Comparing the spectra of compounds **1**, **2** and AmBuPc, red-shifted phthalocyanine Q-band maxima (Q_{max}) are observed in both **1** and **2** relative to the reference compound AmBuPc. This is illustrated in Figure 1. The reciprocal effect

of the 1,8-naphthaimide or 3,4,9,10-perylenebis(dicarboximide) on the B-band maxima (B_{\max}) of phthalocyanine is not apparent but the relative intensity differences between the Q_{\max} and B_{\max} are observable, as indicated in the caption of the figure. The shifts of the Q_{\max} are of the order of 6-7 nm indicative of a moderate through-bond interaction.^{5,9}

On the other hand, their emission spectra also show the two characteristic Q and B bands. However, introducing the fluorescence active chromophore of 1,8-naphthaimide or 3,4,9,10-perylenebis(dicarboximide) in the dyads **1** and **2** significantly increases the intensity of the B band, as shown in Figure 2. The reciprocal effect of the fluorescence active chromophore on the Q band of the spectrum is less apparent but a small blue-shift of the Q_{\max} are observable, from 738 nm to 724 and 719 nm for the compounds AmBuPc, **1** and **2**, respectively.

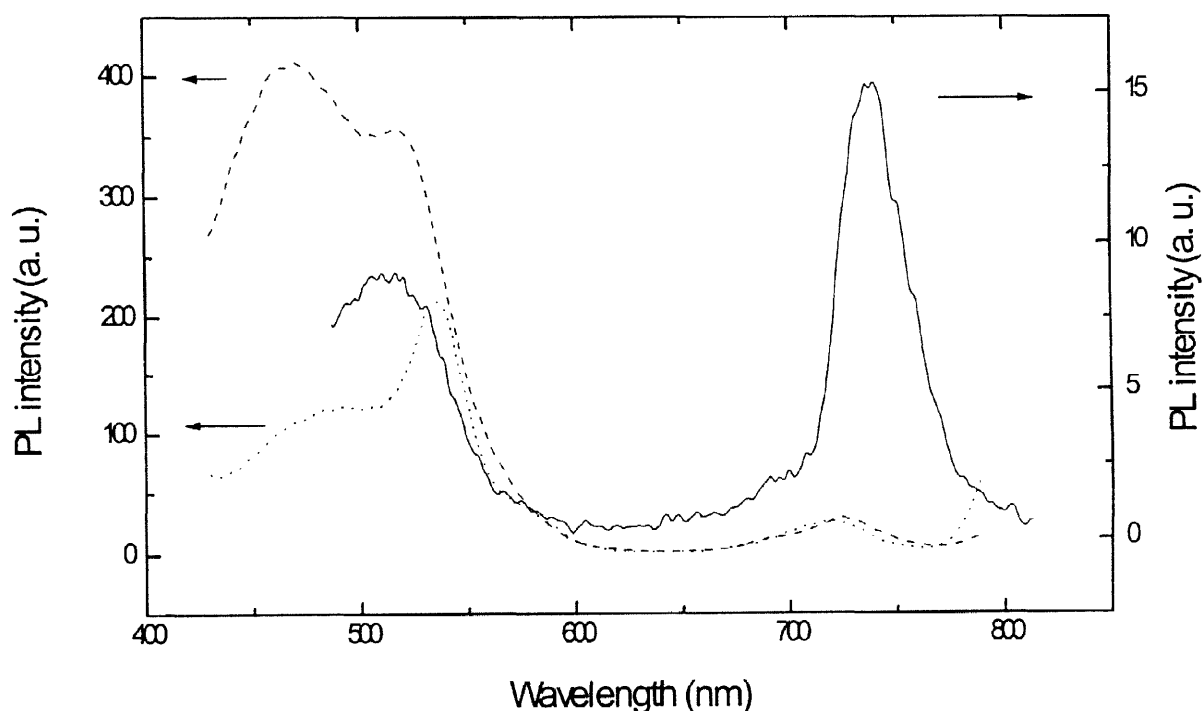


Figure 2. Fluorescence spectra of the compounds **1** (dashed line), **2** (dotted line) and AmBuPc (solid line) recorded on a Perkin-Elmer LS50B fluorescence spectrometer upon 400 nm excitation in chloroform with concentrations of 7.197×10^{-5} (**1**), 8.447×10^{-6} (**2**) and 6.929×10^{-5} (AmBuPc) at room temperature. The relative intensity of B_{\max} and Q_{\max} , *i.e.*, B_{\max}/Q_{\max} values for the compounds **1**, **2** and AmBuPc are about 13.16, 7.93 and 0.60, respectively.

In summary, chromophore modification has been demonstrated in two covalently-linked tri-*tert*-butylphthalocyanine and 1,8-naphthaimide or 3,4,9,10-perylenebis(dicarboximide) conjugates. They have the important features of good solubility in common organic solvents and demonstrable electronic interaction between the chromophores. Further studies indicate that they show good Langmuir-Blodgett film-forming behaviour¹⁰ and strong second-harmonic intensities of the monolayer. Detailed studies are in progress.

References and Notes

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7. a) O'Neil, M.P.; Niemczyk, M.P.; Svec, W.A.; Gosztola, D.; Gaines, G.L.; Wasielewski, M.R. *Science*, 1992, 257, 63; b) Wasielewski, M.R.; Gosztola, D.; Svec, W.A. *Mol. Cryst. Liq. Cryst.*, 1994, 253, 289.
8. Mass spectrum was recorded on a Finigan Mat 90 mass spectrometer in the FD mode. Infrared spectra were recorded on a Perkin-Elmer 2000 infrared spectrometer in the region of 4000-400 cm^{-1} as KBr pellets. UV-Vis spectra were recorded on a Hitachi 340 spectrometer in CHCl_3 solution. Nuclear magnetic resonance spectra for protons were recorded on a DMX 300 spectrometer. Selected data for **1**: FD-MS: m/z (intensity) 697 ($\text{M}^+ - 182 + 2$, 80 %), 877 (M^+ , 100 %). IR (KBr, cm^{-1}): 3290 (w), 2960 (m-s), 2922 (m), 1738 (m), 1668 (m-s), 1618 (m), 1456 (s), 1314 (w), 1257 (w), 1091 (s), 1019 (vs), 888 (w), 831 (vw), 778 (w), 750 (v-m), 670 (w), 467 (m), 392 (w). UV-Vis (chloroform, λ_{max} , nm): 338, 605, 644, 667, 703. $^1\text{H-MNR}$ (CDCl_3 , TMS, δ in ppm): 1.25-1.87 (27 H, CH_3), 7.29-7.99 (18 H, Ar-H). (-7.5)-(-8.5) (2 H, the cavity protons); selected data for **2**: FD-MS: m/z (intensity) 697 (100 %), 1750 (M^+ , 5 %). IR (KBr, cm^{-1}): 3294 (m), 2958 (vs), 2867 (m), 1727 (w), 1618 (vs), 1502 (s), 1483 (s), 1462 (s), 1394 (m), 1363 (m), 1318 (m), 1282 (m), 1258 (m), 1092 (s), 1012 (vs), 913 (w), 893 (w), 829 (w), 759 (m-s), 671 (w), 596 (w), 458 (w), 393 (vw). UV-Vis (chloroform, λ_{max} , nm): 340, 420 (sh), 480 (sh, vw), 520 (vw), 608, 644, 673, 709. $^1\text{H-MNR}$ (CDCl_3 , TMS, δ in ppm): 1.27-1.90 (54 H, CH_3), 7.30-8.90 (32 H, Ar-H). (-7.8)-(-8.9) (4 H, the cavity protons).
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10. From the surface pressure-area isotherms, the limiting area per molecule is estimated to be 63.7 and 205.3 \AA^2 and the collapse pressure is about 30 and 32 mN/m for the compounds **1** and **2**, respectively. The transfer ratio is about 1.0 and 0.6 for the compounds **1** and **2**, respectively. Experimental details refer to [6].