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## Porphyritic phenoxynaphthacenequinones

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### Abstract

The photophysical properties of porphyritic phenoxynaphthacenequinones **1** and **2** were investigated to assess their potential use as gated photoinduced electron transfer systems. Although the photophysical properties of the porphyrin chromophores remain unaltered upon derivatization, the photochemical isomerization of the naphthacenequinone fragment is shut down due to its intimacy with the porphyrin. © 2000 Elsevier Science Ltd. All rights reserved.

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Interest in harnessing light energy has resulted in the development of a large variety of elegant synthetic photoinduced electron transfer (PET) systems incorporating porphyrins as the photoactivated electron donors and quinones as electron acceptors.<sup>1</sup> Our current interest in PET and the use of molecular switches to control molecular-scale electronic devices prompted us to explore the possibility of regulating photoinduced electron transfer by introducing a molecular switching component into porphyritic arrays. The regulation of PET can be potentially accessed using several approaches including the tailoring of: (1) the through-space distance<sup>2</sup> or the through-bond conjugation pathway<sup>3</sup> between the electron donor and acceptor groups; (2) the ability of the porphyrin to act as a reductant; and (3) the ability of the quinone to act as an oxidant. In principle, all of these strategies can take advantage of intrinsic properties of molecular switches.<sup>4</sup> Here we describe two novel porphyrin–phenoxynaphthacenequinone hybrids that target the third approach to regulate PET.

By taking advantage of the fact that phenoxynaphthacenequinones undergo rapid and reversible interconversion between their *trans*- and *ana*-forms when irradiated with appropriate wavelengths of light<sup>5</sup> and by exploiting the expected difference in the reduction potential between the *trans*- and *ana*-forms,<sup>6</sup> a gated photoinduced electron transfer system can be realized. This concept is illustrated in Fig. 1.

The porphyritic phenoxynaphthacenequinone **1a** was conveniently prepared in one step by coupling mono-hydroxytoluoylporphyrin **3**<sup>7</sup> with the known chloronaphthacenequinone **4**<sup>8</sup> (Scheme 1).

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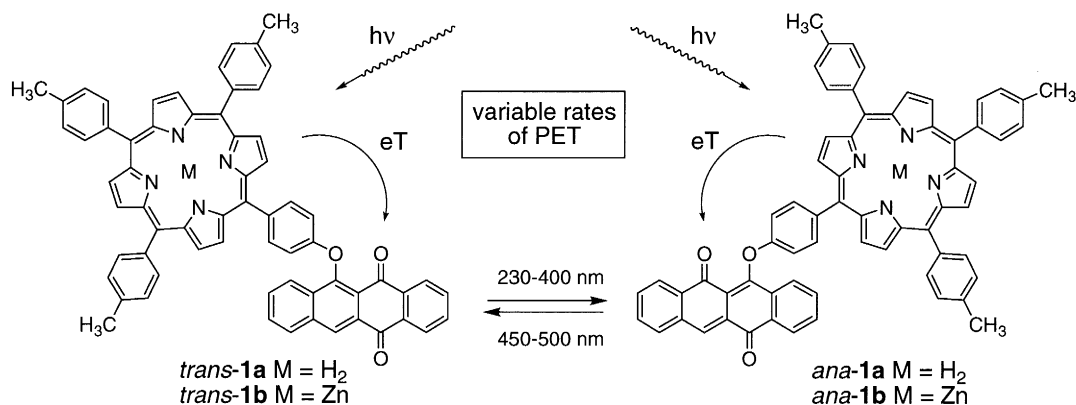
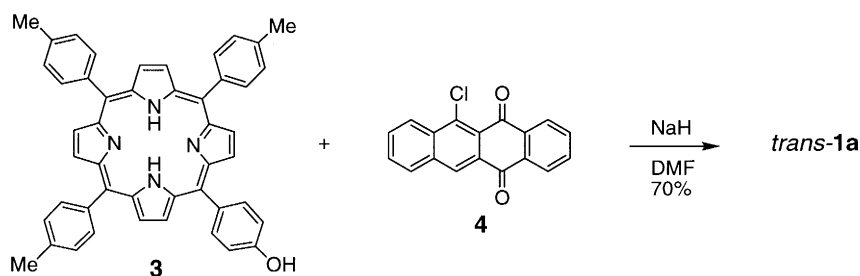
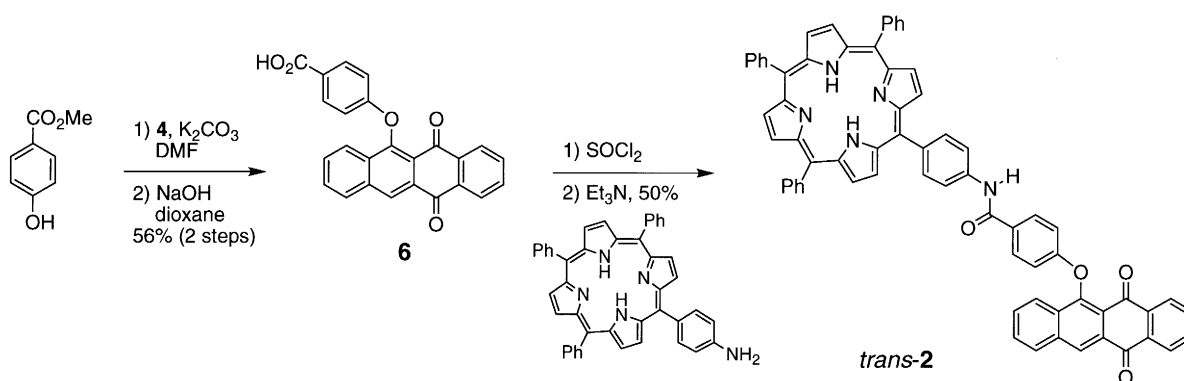


Fig. 1.

The amide-linked analogue **2** was synthesized from carboxyphenoxynaphthacenequinone **6** and 5-(4-aminophenyl)10,15,20-(triphenyl)porphyrin<sup>9</sup> (Scheme 2). All new compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, UV-vis and FT-IR spectroscopy, and mass spectrometry.



Scheme 1.



Scheme 2.

The absorption spectrum of *trans-1a* in the UV-vis region is essentially equivalent to the sum of the absorption spectra of the molecule's components (*trans-5* and tetratolylporphyrin, **TTP**) indicating there is little change in the ground state of either chromophore upon covalent linking (Fig. 2a). Replacing the phenoxy ring on *trans-5* with a *para*-substituted carbomethoxyphenoxy ring and repeating all experiments gave identical photophysical results showing that any inductive effect the porphyrin may have on the system is negligible.

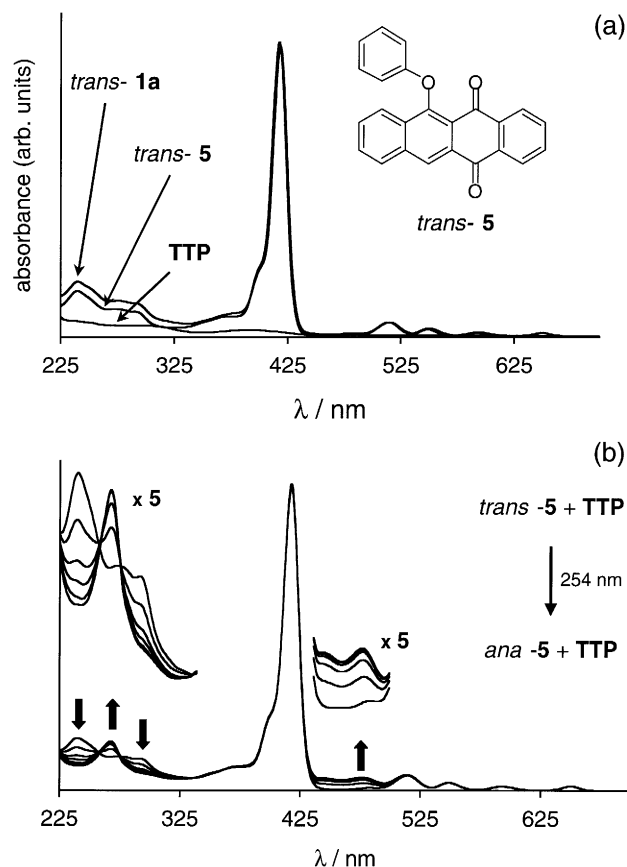


Fig. 2. UV-vis absorption spectra of: (a) **1a**, **5** and **TTP**; (b) an equimolar mixture of **5** and **TTP** showing the photochemical isomerization upon irradiation at 254 nm. All spectra were run in dry degassed THF at  $7.5 \times 10^{-6}$  M

The excited state behavior of **1a**, however, differs significantly from that of its constituents. When **1a** was irradiated with light of wavelengths varying from 240 to 280 nm and from 350 to 380 nm, there was no observable change in the absorption spectrum even under prolonged exposure to high intensity light at several wavelengths within these ranges. To illustrate the expected change in the absorption spectrum, an equimolar mixture of *trans*-**5** and **TTP** was irradiated at 254 or 365 nm (Fig. 2b) which resulted in the rapid disappearance of the absorbance corresponding to the *trans*-isomer of **5** at  $\lambda_{\max}$ =240 (48 000), 292 (39 000) nm and the appearance of the absorbances corresponding to the *ana*-isomer at  $\lambda_{\max}$ =267 (58 000), 476 (16 000) nm. Changing the solvent and concentration, as well as using the metalloporphyrin **1b**,<sup>10</sup> had no effect on the observed behavior. A similar porphyrin-induced inhibition of the photoisomerization of the azobenzene chromophore has been previously reported by Hunter.<sup>11</sup>

Altering the through-bond communication of the porphyrin to the phenoxynaphthacenequinone was explored using amide **2**, which upon photoirradiation resulted in the same inhibition as was observed for **1a** and **1b**.

Clearly, there exists a pathway for the decay of the excited state of the phenoxynaphthacenequinone component in **1** that is faster than the photochemical isomerization reaction. Alternatively, the excited state of the molecular switch may be quenched through an electron/energy transfer process from the phenoxynaphthacenequinone to the porphyrin. These results suggest that the quenching is due to a

through-space and not a through-bond phenomenon. Further photophysical studies are underway to shed light onto this issue.

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