Pergamon

Tetrahedron Letters 40 (1999) 3199–3202

TETRAHEDRON
LETTERS

Enhancement of photoinduced electron-transfer reaction *via* noncovalent bonding: Cooperative effect of a paraquat molecule and zinc(II)phthalocyanine having a macrocyclic ether void

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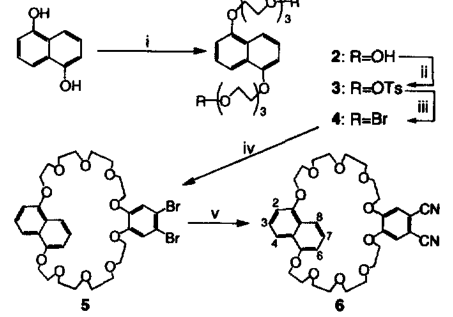
Received 14 December 1998; revised 18 February 1999; accepted 26 February 1999

Abstract: Novel zinc(II)phthalocyanine having a maclocyclic ether void was synthesized. The phthalocyanine interacted with a paraquat molecule at the crown ether void, resulting in the formation of a molecular complex. The fluorescence quenching of the complex was dramatically enhanced because of the intermolecular folding of the paraquat within the crown ether void. © 1999 Elsevier Science Ltd. All rights reserved.

During the past decade, the construction of supramolecular structures utilizing noncovalent bonds such as hydrogen bonding, π-donor-acceptor interaction, and ligand-metal interaction have attracted considerable interest.[1] Some of these supramolecular assemblies are considered to be the artificial model of the photosynthetic reaction centers through the noncovalent interactions between the photosensitizers and the electron carriers.[2] Recently, Willner and co-workers reported a novel approach to efficient, photoinduced electron-transfer reactions through supramolecular complexation between photosensitizers and electron acceptors by π-donor-acceptor interactions.[3] The supramolecular complexation between crown ethers which containing electron-rich aromatic groups and electron-deficient 4,4'-bipyridinium salts through the π-donor-acceptor interaction have been extensively studied by Stoddart and co-workers.[4]

Scheme 1



i, TEGTs, K_2CO_3, LiBr, MeCN, reflux, 24h, 87%; ii, TsCl, THF, NaOHaq., 273K, 2h, 69%; iii, LiBr, acetone, reflux, 24h, 70%; iv,4,5-dibromocatechol, K_2CO_3, DMF, 393K, 35%; v, CuCN, DMF, reflux, 60%

In this communication, we describe the synthesis of novel zinc(II)phthalocyanine complex (1) having an aromatic crown ether void and the photoinduced electron-transfer in supramolecular assemblies composed of the electron acceptor, methylviologen

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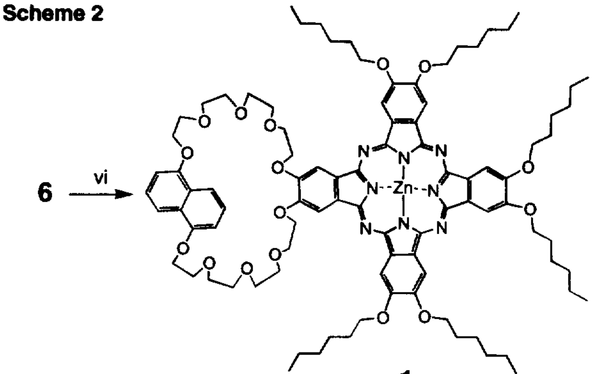
PII: S0040-4039(99)00465-7

bishexafluorophosphate (paraquat, PQT) and the photosensitizer **1**. The association of PQT to the aromatic crown ether void in **1** results in enhancement of the photoinduced electron-transfer reaction within the supramolecular systems.

The new macrocyclic polyether **5** was prepared according to the literature[4] and converted into phthalocyanine precursor **6** (Scheme 1). The synthetic route to asymmetric complex **1** comprises the hybridization process of **6** and three equiv. of 4,5-dihexyloxyphthalonitrile.[5] In an actual procedure, **6** and five equiv. of 4,5-dihexyloxyphthalonitrile were reacted in *n*-hexanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and $ZnCl_2$. The reaction mixture was purified by column chromatography on silica gel by eluting with Et_2O/*n*-hexane/CH_2Cl_2 (8/3/2 v/v/v) and then gradually shifted to Et_2O/*n*-hexane/CH_2Cl_2/MeOH (8/3/2/1 v/v/v/v). The asymmetric complex **1** was isolated by removal of the solvent from the second fraction in 23% yield. The synthesized materials, **1** and **6** were characterized by UV-vis, ^{1}H-NMR, and mass spectroscopy.[6]

Scheme 2



1

vi, 4,5-dihexyloxyphthalonitrile, DBU, $ZnCl_2$, *n*-hexanol, 393K, 23%.

A preliminary experiment using **6** and PQT as a electron donor-acceptor pair clearly indicated the charge-transfer band with absorption maxima around 420 nm.[7] The absorption titration studies of **6** with PQT carried out on the basis of Job's method show the formation of a 1:1 complex.[8] Absorbance change at 420 nm in the titration study using the Benesi-Hildebrand method [9] suggests that the association constant of the complexation between **6** and PQT is 200 M^{-1} at 298 K. The titration studies indicated that the crown ether void containing a naphthalene unit interacted with PQT and acted as a receptor site for PQT in solution.

The zinc(II)phthalocyanine **1** revealed very sharp *Q* and Soret bands typical of zinc(II)phthalocyanines (λ_{max} = 673 nm, log ε = 5.28, $E_{0\text{-}0}$ = 1.85 eV).[10] The absorption spectrum of **1** is almost the same as that of non-crown ether substituted analogue, octakishexyloxyphthalocyaninatozinc(II) (**7**). Upon the addition of PQT to **1**, a charge-transfer band between PQT and the crown ether void of **1** was observed around 420 nm. From comparison of cyclic

Table 1. ^{1}H NMR chemical shift[a] and chemical shift changes ($\Delta\delta$)[b] for **1** and PQT complexation in $CDCl_3/CD_3CN$ (1/1 v/v).

Compound or complex	Pc-*H*	α-Py-*H*	β-Py-*H*	4,8-Np-*H*
	ppm, (Δδ)			
PQT	-	8.95	8.40	-
1	9.01	-	-	8.42
1-PQT	9.00(-0.01)	8.74(-0.21)	8.25(-0.15)	8.08(-0.34)

[a] Pc-*H*: Phthalocyanine ring proton; α-Py-*H*: α- pyridinium proton; β-Py-*H*: β-pyridinium proton; 4,8-Np-*H*: 4- or 8-Naphtyl proton.

[b] $\Delta\delta = \delta_{complex} - \delta_{free}$.

voltammograms for PQT and **1**-PQT mixture, it is apparent that the peak half-width of the PQT^{2+}/PQT^{+} redox wave increased 10 mV by the addition of **1** into PQT. These changes are attributed to the complexation between the crown ether void of **1** and PQT.[4] The ^{1}H NMR measurements also suggest complexation between **1** and PQT (Table 1) . The proton resonance of PQT and the 1,5-naphthyl group in **1** were upfield shifted. On the other hand, proton resonance of the phthalocyanine ring of **1** was not shifted by the addition of PQT. These shifts reveal the formation of an intraannular molecular complex between the crown ether void of **1** and PQT at ground states.[4, 11]

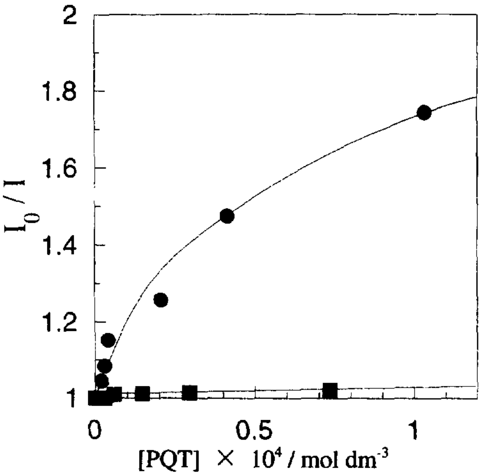


Figure 1. Stern-Volmer plots for the steady-state fluorescence quenching of **1** (●) and **7** (■) by PQT in degassed CH_2Cl_2/CH_3CN = 1/1 v/v mixed solution. Measurement conditions: λ_{ex} = 356 nm, concentration of **1** and **7** are maintained at 3.5 × 10^{-6} mol dm^{-3}.

The zinc(II)phthalocyanine **1** exhibited strong fluorescence in degassed CH_2Cl_2 /MeCN (1/1 v/v) mixed solution at room temperature. The fluorescence spectrum exhibits a strong peak at 680 nm with excitation at 356 nm ($\Phi_F = 0.58$). The linear Stern-Volmer plots for **7** indicate that the weak fluorescence quenching of **7** is fully dominated by a diffusion process. In contrast, the nonlinear Stern-Volmer plots for **1** suggest that the electron-transfer quenching of photosensitizer **1** by PQT proceeds through a complexation process that is attributed to static quenching of **1** by PQT (Figure 1).[3] The association constant of **1** and PQT from the Scatchard-type equation using fluorescence quenching data reveals good agreement with that from UV-vis absorption studies.[12] This suggested that the static process plays a key role in fluorescence quenching in the assembly between **1** and PQT. From the energy for 0-0 transition of **1** ($E_{0\text{-}0}$ = 1.85 eV), the oxidation potential of **1** ($E(D/D^+)$ = 680 mV vs. SCE), and the reduction potential of PQT ($E(A/A^-)$ = - 450 mV vs. SCE) which obtained from spectroscopic and electrochemical studies, the thermodynamic driving force (ΔG) for the photoinduced electron-transfer from **1** to PQT was calculated to be – 0.64 eV, ignoring Coulombic terms.[13] This indicates that the intermolecular electron-transfer in the assembly is thermodynamically favored. The results obtained from fluorescence quenching studies of **1** with PQT suggest that the electron-transfer is intensified dramatically by the crown ether void of **1**.

In conclusion, we have demonstrated that enhancement of the electron-transfer reaction from zinc (II)phthalocyanine **1** to PQT was accomplished by the noncovalent bonding between the crown ether void and PQT through π-donor-acceptor interaction. The supramolecular complexation is available for the development of new catalytic systems as efficient energy conversion systems.

Acknowledgements: This research was supported by a Grant-in-Aid for COE research "Advanced Fiber/Textile Science and Technology" from the Ministry of Education, Science, Sports, and Culture of Japan (#10CE2003). We thank Professor N. Kobayashi of Tohoku University for assistance with mass spectroscopy.

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6) *Selected data* for **1**: ^{1}H-NMR (400 MHz, CDCl$_3$, 25℃): δ = 8.98 (d, J = 0.27 Hz, 8H, phthalocyanine ring), 8.40-8.19 (br, 2H, Np 4,8-H), 6.81-6.69 (br, 2H, Np 3,7-H), 6.20-5.88 (br, 2H, Np 2,6-H), 4.31-3.35 (m, 32H, OCH$_2$), 2.12 (s, 8H, OCH$_2$), 1.92-1.85 (t, 8H, CH$_2$), 1.75 (s, 14H, CH$_2$), 1.52-1.25 (m, 18H, CH$_3$), 1.02-0.92 (m, 30H, CH$_2$); FAB-MS: *m/z* = 1687 (Nitrobenzyl alcohol matrix); MALDI-TOF-MS: an isotopic peaking at *m/z* = 1687.7 (2'-4'-6'-Trihydroxyacetophenone monohydrate matrix) (**1** requires 1687.38). *Selected data* for **6**: FT-IR (KBr): 2232 cm^{-1} (CN); ^{1}H-NMR (400 MHz, CDCl$_3$, 25℃): δ = 7.77 (d, J = 0.24 Hz, 2H, Np 4,8-H), 7.34 (d, J = 0.16 Hz, 2H, Np 3,7-H), 7.28 (s, 2H, Ph), 6.92 (d, J = 0.12 Hz, 2H, Np 2,6-H), 4.28-3.38 (m, 32H, OCH$_2$); MALDI-TOF-MS: *m/z* = 658.54 ([2-(4-Hydroxyphenylazo)benzoic acid matrix) (**6** + Na$^+$ requires 658.33).

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