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Short communication

Synthesis and spectroscopic investigation of trifluoroethoxy-coated phthalocyanine linked with fullerene

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ABSTRACT

Synthesis and spectroscopic investigation of trifluoroethoxy-coated phthalocyanine–fullerene dyad **2** has been described. While nonfluorinated phthalocyanine–fullerene dyad **1** showed an efficient property of intramolecular photoinduced electron transfer, dyad **2**, regardless of its covalently linked dyad system, appears not to show any electronic communication between fullerene and phthalocyanine. This observation is presumably due to the strong electron withdrawing nature of 12 trifluoroethoxy groups; fluorine leads phthalocyanine to become an acceptor whose electronic accepting property is equivalent to that of fullerene. This is a unique example that fluorine can terminate electronic communication in the covalently fullerene–phthalocyanine dyad system.

1. Introduction

Much attention has been paid to phthalocyanines and porphyrins covalently linked with fullerenes via different spacers to develop novel materials for artificial photosynthetic systems such as solar cells in nanotechnology [1–3]. Selection and combination of electron donor dyes with acceptor fullerenes play a key role in photovoltaic devices and a variety of porphyrin and fullerene linked dyads have been reported so far. On the other hand, the chemistry of phthalocyanine-based fullerene dyads is still a developing field and phthalocyanines are expected to be much more efficient due to their intense absorption in the UV/violet and in the red/near-IR spectral regions as well as electrochemical and photochemical stabilities. Linβen et al. initially reported a covalently bonded fullerene–phthalocyanine complex in 1995 [4]. Since then, interest in covalently bound fullerene-functionalized phthalocyanines has been increasing. Nowadays, several unsymmetrical metal phthalocyanine–fullerene conjugates via a flexible [5,6] or rigid [7–13] linker have been synthesized to study intramolecular processes such as electron and energy transfers between phthalocyanines and fullerenes. We recently disclosed a novel unsymmetrical metal phthalocyanine–fullerene dyad **1** for the development of thin film solar cells, in which fullerene is covalently bonded to a terminal position of phthalocyanine via a saturated alkyl chain. UV–vis and steady-state fluorescence spectra studies of **1** revealed that intramolecular, and not intermolecular, photoinduced electron transfer was observed in the solution state [14].

As an extension of this study, and in connection with our research program aimed at designing and synthesizing functional phthalocyanines [15–18], we were interested in a novel unsymmetrical trifluoroethoxy-coated metal phthalocyanine–fullerene dyad **2**. The control and suppression of electronic communication of fullerene dyads only by their inherent specificity without any external source is a challenge in materials science [1–3]. We expected that the oil repellence [15,17] and electron withdrawing effects of 12 trifluoroethoxy groups at peri positions of phthalocyanine in dyad **2** should terminate the electronic communication to fullerene. In this paper, we disclose the synthesis and properties of the trifluoroethoxy-coated metal phthalocyanine–fullerene dyad **2**. Inspection of the UV–vis and fluorescence spectra and electrochemical measurements revealed new and interesting aspects of dyad **2** in which no electronic communication between phthalocyanine and fullerene in this dyad was observed (Fig. 1).

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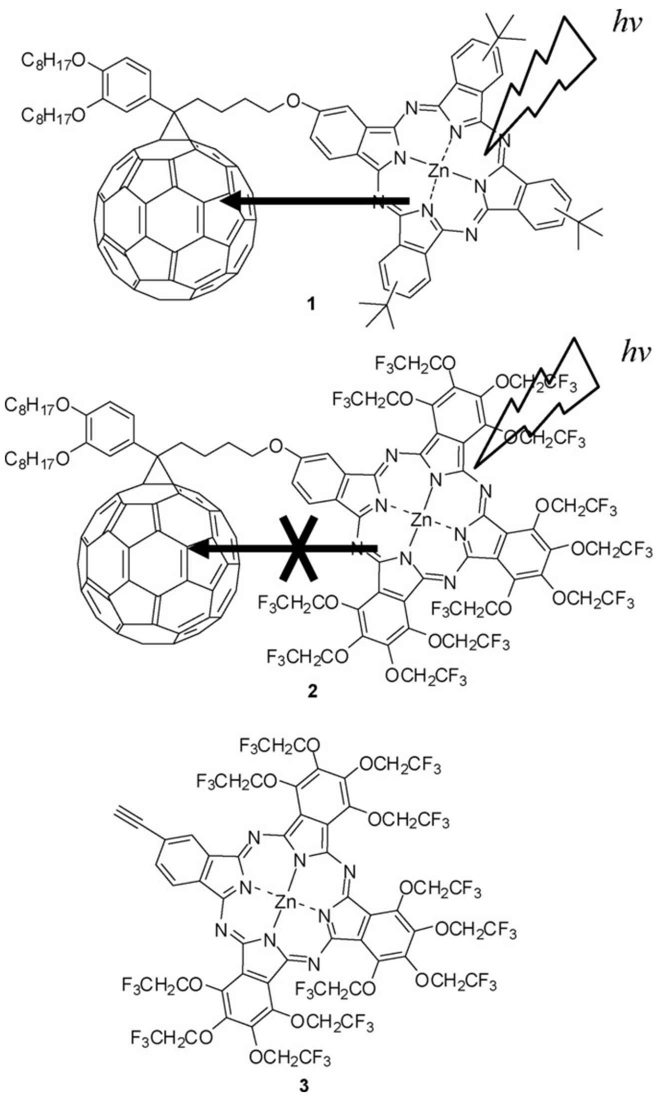


Fig. 1. Phthalocyanine–fullerene dyad **1**, trifluoroethoxy-coated dyad **2** and trifluoroethoxy-phthalocyanine **3**.

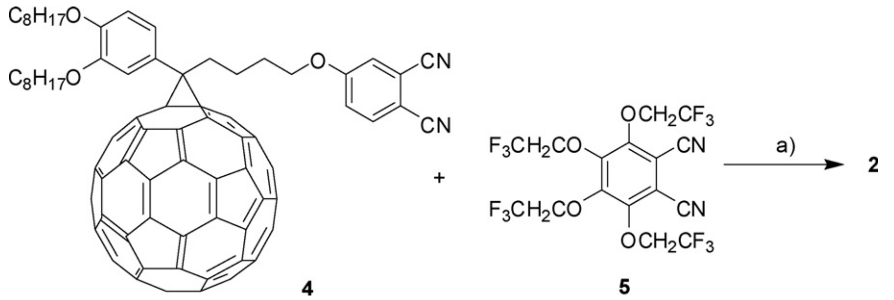
2. Results and discussion

The synthesis of trifluoroethoxy-coated phthalocyanine–fullerene dyad **2** is shown in Scheme 1. Fullerene phthalonitrile **4** [14] was treated with excess equivalents of trifluoroethoxy-coated phthalonitrile to react with zinc chloride in 2-dimethylaminoethanol at 130 °C for 24 h. The crude product was purified by column chromatography on silica gel eluted with CH_2Cl_2:ethanol = 98:2 to 90:10 to furnish **2** as a dark green solid; its identity and purity were confirmed by ^1H NMR and analytical reverse-phase HPLC. MALDI-TOF MS spectrum of **2** shows the isotopic distribution caused by Zn(II), which provides proof for its characterization (Figs. 2 and 3).

The phthalocyanine–fullerene dyad **2** is soluble in *o*-DCB, THF, DMF, 1,4-dioxane, acetonitrile, CH_2Cl_2, $CHCl_3$ and pyridine. As expected, the UV–vis spectrum of **2** in THF showed a Q-band at 706 nm and a Soret band at 314 nm, which indicates that dyad **2** exists as an aggregation-free monomer in solution. The Q-band did not split in spite of the unsymmetrical nature of substituted phthalocyanines [19]. The UV–vis spectrum of **2** is a superposition of those of **3** and **4**. These results confirmed that the fullerene moiety has less effect on the electronic structure of phthalocyanine in the ground state (Fig. 4). These observations are in agreement with the previously reported results of the UV–vis spectrum of **1** [14].

We next investigated the fluorescence spectra (Fig. 5). It is interesting to note that the previously reported phthalocyanine–fullerene dyad **1** showed remarkably quenched fluorescence spectra about 88% due to an efficient photoinduced electron transfer from phthalocyanine as a donor to fullerene as an acceptor [14]. Namely, while reference symmetrical tetra-*tert*-butyl phthalocyanine showed strong fluorescence at 677 nm (fluorescence quantum yield, $\Phi_f = 0.58$), the fluorescence quantum yield (Φ_f) of **1** was 0.07 at 687 nm regardless of the non-aggregation. On the other hand, the emission of trifluoroethoxy-coated **2** was not quenched at all ($\lambda_{em} = 722$ nm; $\Phi_f = 0.17$). This non-quenching is supported by the result that reference unsymmetrical mononuclear trifluoroethoxy-coated phthalocyanine **3** [17] also showed a similar intense fluorescence at 709 nm ($\Phi_f = 0.18$) independent of the addition of fullerene (**3**:fullerene = 1:0 to 1:10). These results indicate that there is no electronic communication between the phthalocyanine moiety and fullerene in trifluoroethoxy-coated **2** in the excited state. This phenomenon is very unique and can be explained by the fact that the strong electron withdrawing nature of trifluoroethoxy groups stops the intramolecular electron and/or charge transfer from phthalocyanine to fullerene. Phthalocyanines generally act as electron donors in the fullerene dyad system; nevertheless, because of its greater electronegativity, fluorine leads phthalocyanine to be an acceptor whose electron accepting nature is equivalent to that of fullerene. Although a variety of phthalocyanine–fullerene dyads has been reported, to our knowledge, this is a rare example of phthalocyanine–fullerene dyads which realizes no intramolecular electronic communication between phthalocyanine and fullerene in the covalently linked system.

Finally, electrochemical studies were measured by differential pulse voltammetry (DPV) using a platinum electrode in THF (Fig. 6, Table 1). The results were compared with those of **3** and **4** as reference compounds. Although the DPV of **2** was rather broad and oxidation potentials were not really clear, the reduction potentials



Scheme 1. a) 3,4,5,6-Tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (**5**, 19 equiv), $ZnCl_2$, 2-dimethylaminoethanol, 130 °C, 7%.

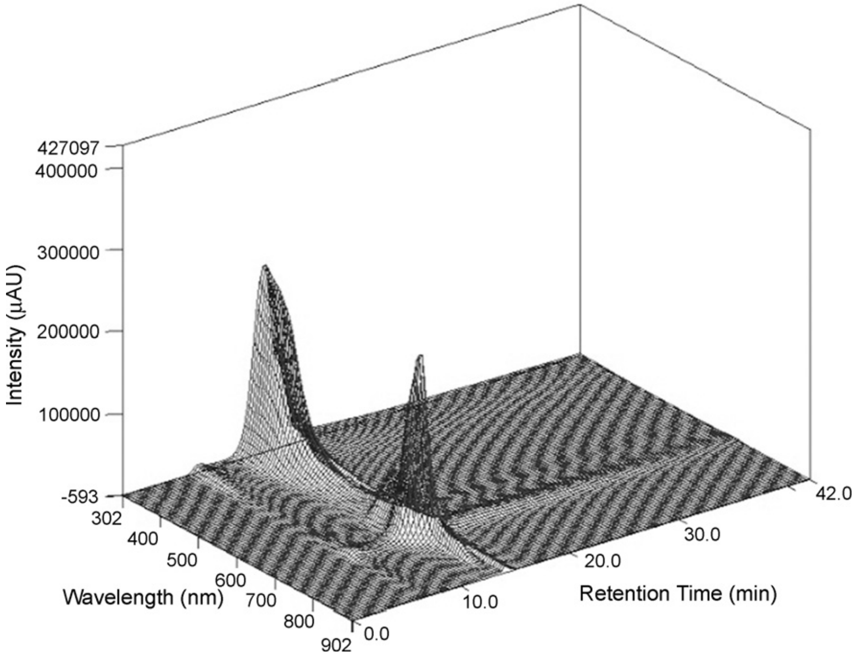


Fig. 2. HPLC spectrum of **2**: (H_2O:MeCN:THF = 8:42:50, 0.2 mL/min), t_R = 14.1 min.

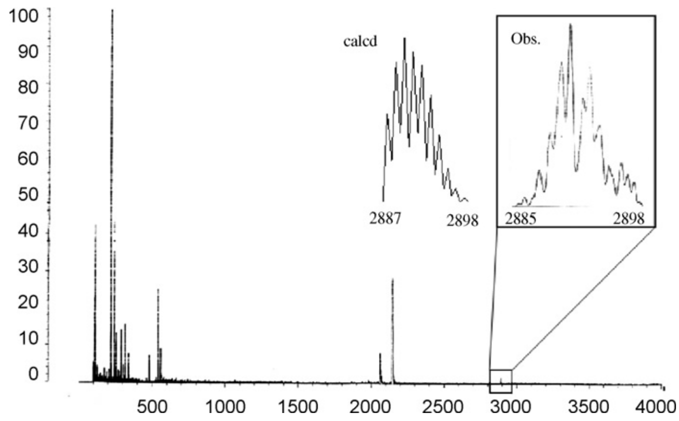


Fig. 3. MALDI-TOF MS chart of **2** (DHB): m/z = 2887–2898 ($[M + H^+]$, isotopic pattern).

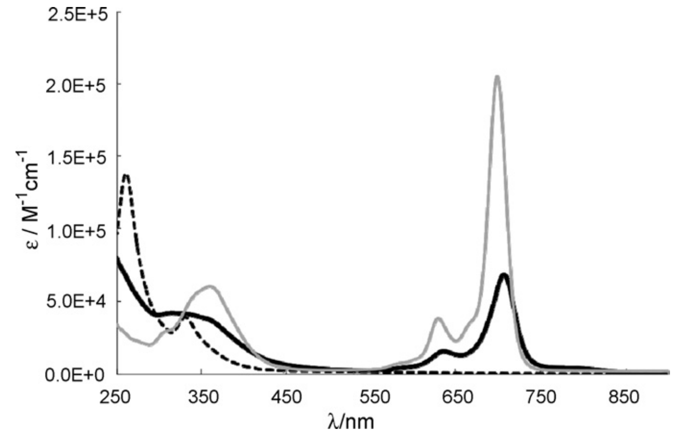


Fig. 4. UV–vis spectra of **2** (solid line), **3** (gray line) and **4** (dashed line) in THF.

of dyad **2** compared with a superposition of those of **3** and **4** were basically similar. This suggests that no electronic coupling prevails between the two electroactive groups of dyad **2** in their singlet ground state.

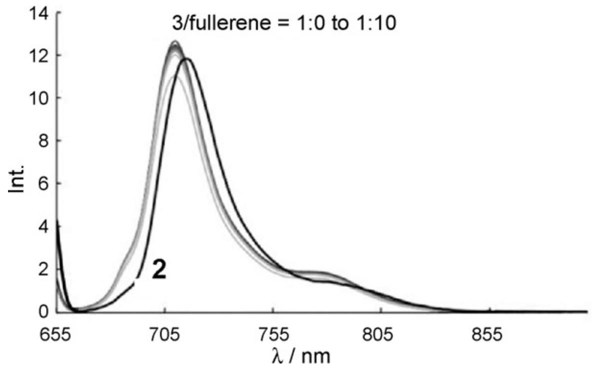


Fig. 5. Fluorescence spectra of **2**, **3** and mixture of **3**/fullerene (**3**:fullerene = 1:0 to 1:10) in THF.

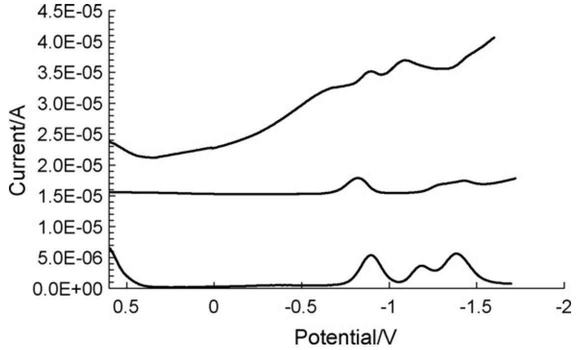


Fig. 6. Differential pulse voltammograms of **2** (top), **4** (middle), and **3** (bottom).

Table 1
Peak potentials (mV vs Ag/$AgNO_3$) of **2**, **4**, and **3**.

	E_{ox}	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^3
2	0.645	−0.800	−1.000	−1.360	−1.530
4		−0.800	−1.265	−1.410	
3	0.610	−0.900	−1.185	−1.380	

3. Conclusion

In conclusion the synthesis and spectral investigation of trifluoroethoxy-coated phthalocyanine–fullerene dyad **2** has been described. Dyad **2**, regardless of its covalently linked system, appears not to show any electronic communication between fullerene and phthalocyanine. It is reported that the trifluoroethoxy groups of similar unsymmetrical phthalocyanines serve *electron donor groups* in a conjugated donor–acceptor dyad system [20]. In addition to this, fullerene always acts as *an electron acceptor* in fullerene dyad systems such as phthalocyanine–fullerene dyads [4–13], porphyrine–fullerene dyads [2,3] and perylene–fullerene dyads [21]. It is interested to note that fullerene does not serve an electron acceptor substituent in our donor–acceptor dyad **2**. This is a unique example in which fluorine can stop intramolecular electronic communication even in the covalent phthalocyanine–fullerene dyad system. Although the net effects of trifluoroethoxy moiety in the **2** is not clear, this result could be useful for the construction of novel electron communication network systems.

4. Experimental

Fullerene-(TFEO)$_3$Pc dyad **2**: A mixture of **4** (63 mg, 0.050 mmol), 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (**5**, 494 mg, 0.95 mmol), ZnCl$_2$ (19 mg, 0.30 mmol) and 2-dimethylaminoethanol (0.5 mL) was refluxed for 24 h. After cooling to room temperature, water was added, then filtered followed by washing with water. Crude product was purified by column chromatography (silica gel; CH$_2$Cl$_2$:ethanol = 98:2 to 90:10), to yield **2** (10.1 mg, 7%) as greenish solids. ^{1}H NMR (THF-d_8, 200 MHz): δ 9.81 (brs, 1H), 9.21 (brs, 1H), 8.78 (brs, 1H), 6.50–7.78 (brm, 3H), 5.56 (brs, 4H), 4.45–4.95 (brm, 20H), 3.93 (brs, 6H), 1.18 (brs, 30H), 0.78 (brs, 6H); ^{19}F NMR (THF-d_8, 188 MHz): δ-74.4 (brm, 36F); FT-IR (KBr): 662, 753, 833, 970, 1068, 1161, 1274, 1454, 1606, 1720, 2855, 2930, 3378; UV–vis (1.0×10^{-5} M in THF): λ_{max} ($\log\varepsilon$) = 314 (4.62), 635 (4.18), 706 (4.84) nm; fluorescence (THF): λ_{em} = 664, 722 nm, Φ_f = 0.17; MALDI-TOF MS (DHB): m/z = 2888–2898.

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