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Energy Transfer Processes in Novel Subphthalocyanine–Fullerene Ensembles

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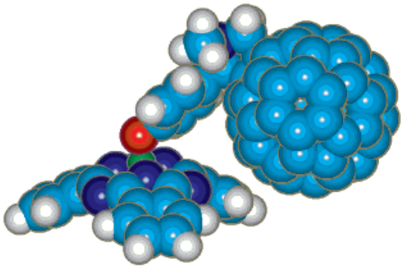
ABSTRACT



A series of subphthalocyanine–C_{60} dyads in which the two subunits are placed at different distances have been prepared and their electrochemical properties measured. Photophysical measurements reveal energy transfer events following the initial photoexcitation of the subphthalocyanine chromophore.

Subphthalocyanines[1] (SubPcs) are nonplanar[2] aromatic macrocycles that differ from their higher homologues, phthalocyanines,[3] in that they comprise three isoindole units around a boron atom. Whereas SubPcs have shown very interesting photophysical properties,[2e,4] their ability to promote intramolecular charge or energy transfer processes, when included in electroactive dyads, remains unexplored. Regarding the design of novel photo- and electroactive donor−acceptor

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(1) (a) Geyer, M.; Plenzig, F.; Rauschnabel, J.; Hanack, M.; del Rey, B.; Sastre, A.; Torres, T. *Synthesis* **1996**, 1139−1151. (b) Claessens, C. G.; González-Rodríguez, D.; Torres, T. *Chem. Rev.* **2002**, in press.

(2) (a) Kietaibl, H. *Monatsh. Chem.* **1974**, *105*, 405−418. (b) J. Rauschnabel, J.; Hanack, M. *Tetrahedron Lett.* **1995**, *36*, 1629−1632. (c) Kasuga, K.; Idehara, T.; Handa, M.; Ueda, Y.; Fujiwara, T.; Isa, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2559−2563. (d) Engel, M. K.; Yao, J.; Maki, H.; Takeuchi, H.; Yonehara, H.; Pac, C. *Report Kawamura Inst. Chem. Res.* **1998**, *9* (*Vol. Date 1997*), 53−65. (e) Ho Kang, S.; Kang, Y. S.; Zin, W. C.; Olbrechts, G.; Wostyn, K.; Clays, K.; Persoons, A.; Kim, K. *Chem. Commun.* **1999**, 1661−1662. (f) Claessens, C. G.; Torres, T. *Tetrahedron Lett.* **2000**, *41*, 6361−6365.

(3) (a) *Phthalocyanines: Properties and Applications*; Leznoff, C. C.; Lever, A. B. P., Eds.; VCH: Weinheim, 1989, 1993, 1996; Vols 1−4. (b) Hanack, M.; Heckman, H.; Polley, R. In *Methods in Organic Chemistry (Houben-Weyl)*; Schauman, E., Ed.; Georg Thieme Verlag: Stuttgart, 1998; Vol. E 94, p 717. (c) de la Torre, G.; Nicolau, M.; Torres, T. In *Phthalocyanines: Syntheses, Supramolecular Organization and Physical Properties* (*Supramolecular Photosensitive and Electroactive Materials*); Nalwa, H. S., Ed.; Academic Press: New York, 2001; pp 1−111.

(4) (a) del Rey, B.; Keller, U.; Torres, T.; Rojo, G.; Agulló-Lopez, F.; Nonell, S.; Martí, C.; Brasselet, S.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1998**, *120*, 12808−12817. (b) Sastre, A.; Torres, T.; Diaz-Garcia, M. A.; Agulló-Lopez, F.; Dhenaut, C.; Brasselet, S.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1996**, *118*, 2746−2747. (c) Kitagawa, S.; Shinkai, M.; Nanba, N.; Yoshimura, E. E. Jpn. Kokai Tokyo Koho JP 09,131,968 [97,131,968], 1997; *Chem. Abstr.* **1997**, *127*, 1277.

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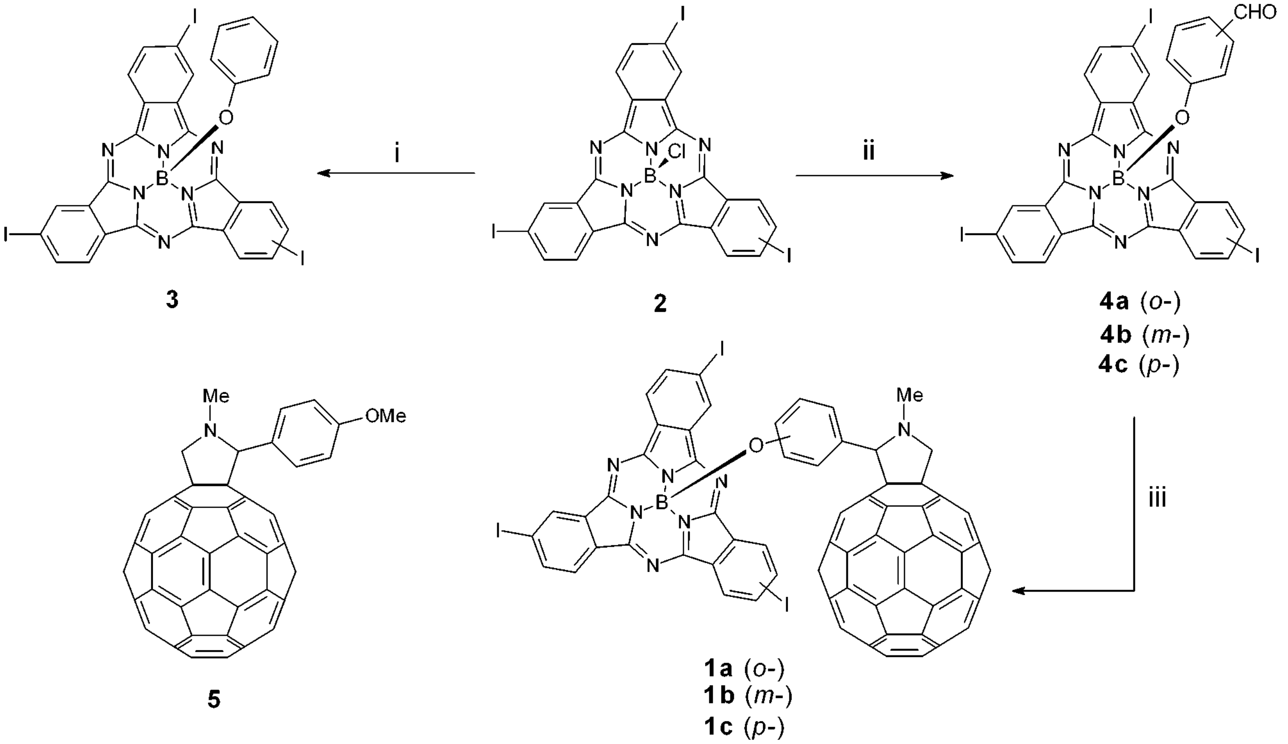
Scheme 1. Synthesis of SubPc−C_{60} Dyads **1a−c** from the Corresponding Formyl-Substituted SubPcs **4a−c**[a]



[a] Reagents and Conditions: (i) phenol, toluene, 110 °C, 70%; (ii) *o*-, *m*-, or *p*-hydroxybenzaldehyde, toluene, 110 °C, 55−68%; (iii) C_{60}, sarcosine, toluene, 100 °C, 43−58%.

ensembles, much attention has been focused on C_{60} as an electron acceptor due to its unique structure and redox properties, which result in improved charge-separation behavior.[5] We report herein the synthesis, electrochemistry, and photophysics of three different SubPc−C_{60} dyads (**1a−c**), in which the average distance between the two subunits is regulated by the nature of the spacer (i.e., variation of the phenyl substitution from ortho to meta to para).

SubPc **2** is obtained as a mixture of two regioisomers by cyclotrimerization of 4-iodophthalonitrile in the presence of boron trichloride. The substitution of the axial chlorine group by phenol or *o*-, *m*-, or even *p*-hydroxybenzaldehyde led to SubPcs **3**, **4a**, **4b** and **4c**, respectively (Scheme 1). Dyads **1a−c** were synthesized from the formyl-substituted SubPcs **4a−c** by an azomethine ylide 1,3-dipolar cycloaddition to C_{60}.[6] Compound **5** was obtained in a similar way from *p*-methoxybenzaldehyde and C_{60}.

Compounds **1−5** were fully characterized by ^{1}H and ^{13}C NMR, FTIR, MALDI-MS, and UV−vis spectroscopy.[7] The three dyads are in fact a mixture of two diastereoisomers, and this is manifested by the splitting of some signals in their ^{1}H NMR spectra. Remarkably, the signals of the protons in the phenyl spacer are shifted considerably upfield (7.2 and 5.4 ppm for **1c**) as a consequence of the SubPc ring-current. The UV−vis spectra of the dyads already reveal intramolecular electronic interactions in the ground state

Table 1. Oxidation Peaks Potentials and $\epsilon_{1/2}$ Data (in mV and vs Ferrocene) of SubPc−C_{60} Dyads and Their Reference Compounds

compound	$\epsilon^{2}_{\mathrm{p,\,ox}}$	$\epsilon^{1}_{\mathrm{p,\,ox}}$	$\epsilon^{1}_{1/2}$	$\epsilon^{2}_{1/2}$	$\epsilon^{3}_{1/2}$
1a		+822	−1016	−1393	−1560
1b	+998	+779	−1004	−1347	−1511
1c	+1038	+854	−1037	−1380	−1567
3		+821	−1323		
5			−910	−1435	−2019

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[5] (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Martin, N.; Sanchez, L.; Illescas, B.; Perez, I. *Chem. Rev*, **1998**, *98*, 2527. (c) Hirsch, A. In *The Chemistry of the Fullerenes*; Georg Thieme Verlag: Stuttgart, 1994. (d) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.*, **1999**, 2445−2457. (e) Guldi, D. M. *Chem. Commun.* **2000**, 321−327.

[6] Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

[7] Selected data for **1a**: ^{1}H NMR ($CDCl_3/CS_2$ (1: 1), 300 MHz): δ 9.2−9.1 (m 3H), 8.6−8.5 (m 3H), 8.2−8.1 (m 3H), 7.4−7.3 (m 1H), 6.8−6.6 (m 1H), 5.8−5.7 (m 1H), 5.4−5.3 (m 1H), 4.9−4.7 (m 1H), 4.6−4.4 (m 1H), 4.2−4.0 (m 1H), 2.3 (s 3H). MALDI-TOF *m/z*: 1641 [M^+]. UV−vis ($CHCl_3$): λ_{max} (log ϵ) = 575 (4.2), 525 (sh), 430 (2.7). **1b**: ^{1}H NMR ($CDCl_3/CS_2$ (1: 1), 300 MHz) δ: 9.2−9.1 (m 3H), 8.6−8.5 (m 3H), 8.2−8.1 (m 3H), 7.2−7.1 (m 1H), 6.8−6.7 (m 1H), 5.8−5.7 (m 1H), 5.4−5.3 (m 1H), 5.0−4.8 (m 1H), 4.6−4.5 (m 1H), 4.2−4.1 (m 1H), 2.6 (s 3H). UV−vis ($CHCl_3$): λ_{max} (log ϵ) = 573 (4.1). **1c**: ^{1}H NMR ($CDCl_3/CS_2$ (1: 1), 300 MHz) δ: 9.1−9.0 (m 3H), 8.5−8.4 (m 3H), 8.2−8.1 (m 3H), 7.2 (m 2H), 5.4 (m 2H), 4.8 (d 1H), 4.6 (s 1H), 4.1 (d 1H), 2.6 (s 3H). UV−vis ($CHCl_3$): λ_{max} (log ϵ) = 572 (4.2).

Table 2. Selected Photophysical Data of SubPc–C_{60} Dyads and Their Reference Compound in Toluene

feature	**3**	**1a**	**1b**	**1c**
absorption maxima (λ_{max})	571 nm	575 nm	574 nm	572 nm
fluorescence maxima (λ_{max}); SubPc	585 nm	596 nm	592 nm	591 nm
fluorescence maxima (λ_{max}); C_{60}		715 nm	715 nm	715 nm
fluorescence quantum yield (Φ); SubPc	0.08	5.0×10^{-4}	9.6×10^{-4}	1.9×10^{-3}
fluorescence quantum yield (Φ); C_{60}		6.0×10^{-4}	4.8×10^{-4}	5.1×10^{-4}
energy transfer efficiency		100%	80%	85%
fluorescence lifetime (τ); SubPc	0.51 ns	not detectable	not detectable	not detectable
fluorescence lifetime (τ); C_{60}		1.23 ns	1.17 ns	1.26 ns
singlet lifetime (τ); SubPc	0.59 ns	0.029 ns	0.041 ns	0.061 ns
	1.7×10^{9} s^{-1}	3.4×10^{10} s^{-1}	2.4×10^{10} s^{-1}	1.6×10^{10} s^{-1}
singlet lifetime (τ); C_{60}		1.11 ns	1.14 ns	1.25 ns

between the two subunits. Thus, the Q-band of the SubPc unit shows a red shift of a few nanometers in dyads **1a**–**c** compared to that of **3** (Table 2).

The electrochemistry of compounds **1a**–**c**, **3**, and **5** was carried out in THF containing 0.1 M $TBPF_6$ under high-vacuum conditions. The THF was vapor transferred directly into the electrochemical cell from a sodium–potassium amalgam (Na–K). A glassy carbon (3 mm) was used as the working electrode, a silver wire as a pseudo-reference, and a platinum wire as the auxiliary electrode. All electrochemical measurements were performed using a BAS 100B electrochemical instrument. The cyclic voltammograms of the compounds are shown in Figure 1, and the electrochemical data are summarized in Table 1.

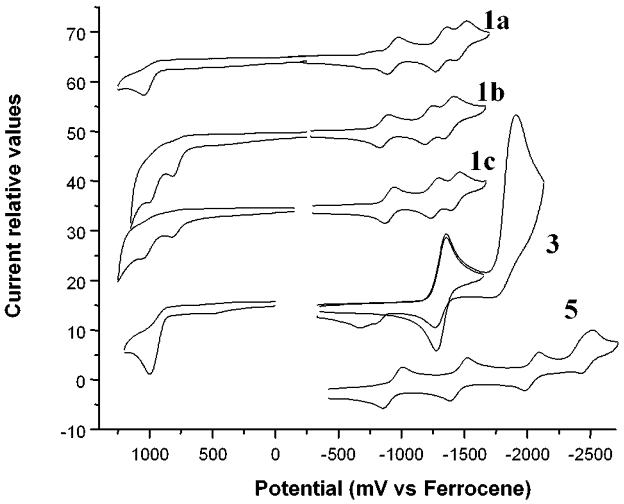

Figure 1. Cyclic voltammograms of SubPc–C_{60} dyads and their reference compounds (0.5 mM) in THF and 0.1 M $TBPF_6$ as a supporting electrolyte.

For dyads **1a**–**c**, the waves at $\epsilon^1_{1/2}$ and $\epsilon^3_{1/2}$, one electron each, are assigned to the C_{60} core and the waves at $\epsilon^1_{p,ox}$ and $\epsilon^2_{1/2}$ to the SubPc group. These data indicate that **1b** is the easiest to reduce and also the easiest to oxidize in the series, indicating the weakest ground-state interaction between the donor and acceptor groups in the series. This suggests that in the ground state, the electronic effects that dominate are through-bond and not through-space, since they follow the expected (and similar) behavior for the ortho and para, and the weakest electronic effect for the meta isomer.[8] Therefore, in the ground state (ortho and meta isomers), these compounds probably have the SubPc group far from the fullerene core, via rotation about the phenyl spacer. Thus, ground-state and excited-state conformations are probably substantially different, with closer D–A approach in the latter.

Figure 1 also shows an irreversible many-electron wave reduction (~3e) for compound **3** with an ϵ_p value around −1900 mV. A similar wave is observed for dyads **1a**–**c** (not shown) and corresponds to subsequent reductions of the SubPc unit. The irreversibility seems to be due to chemical reactions following multiple electron reductions.

Irreversible oxidations are also observed for both the first and second anodic processes for dyads **1b** and **1c**, as shown in Figure 1. The second oxidation wave, at $\epsilon^2_{p,ox}$, seems to correspond to the oxidation of the nitrogen in the pyrrolidine ring attached to the C_{60} group. For the other compounds, this wave was close to the solvent threshold and was barely observed. The data in Table 1 indicate that the SubPc group in **1b** is easier to oxidize with an $\epsilon_{p,ox}$ of +779 mV, even easier than its reference compound **3** with an $\epsilon_{p,ox}$ of +821 mV.

In general, subphthalocyanines are strong fluorophores with quantum yields close to unity, which, in turn, renders them ideal probes for intramolecular electron/energy transfer reactions. Importantly, the strong fluorescence[9] of the subphthalocyanine chromophore in **3** ($\lambda_{max} = 585$ nm; $\Phi = 0.08$) is subject to a marked quenching in dyads **1a**–**c**, with quantum yields typically on the order of $(7.5 \pm 2.5) \times 10^{-4}$ (see Table 2). Although at the chosen 570 nm excitation wavelength the fullerene absorption ($\epsilon_{570\ nm} \sim 2.000\ M^{-1}cm^{-1}$)

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(8) Sumner, J. J.; Creager, S. E. *J. Am. Chem. Soc.* **2000**, *122*, 11914–11920.

(9) Emission spectra were recorded with an SLM 8100 spectrofluorometer. The experiments were performed at room temperature. A 570 nm long-pass filter in the emission path was used in order to eliminate the interference from the solvent and stray light for recording the subphthalocyanine/fullerene fluorescence. Each spectrum was an average of at least 5 individual scans, and the appropriate corrections were applied.

plays an irrelevant role, relative to the strong absorption of the subphthalocyanine ($\epsilon_{570\ \mathrm{nm}} \sim 50.000\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$), the near-infrared part of the emission spectrum revealed the characteristics of the fullerene fluorescence ($\lambda_{\max} = 715$ nm). A reasonable rationale for this observation implies a rapid transfer of singlet excitation energy. Employing reference **5** with matching absorption at the excitation wavelength helped to quantify the fullerene fluorescence quantum yields: the Φ-values nearly approach that measured for reference **5** (6.0×10^{-4}) and, thus, corroborate high efficiencies.

Decisive evidence for the origin of the fullerene fluorescence was obtained from an excitation spectrum. In fact, the excitation spectra of all dyads (**1a−c**) were exact matches of (i) that recorded for subphthalocyanine reference **3** and (ii) the subphthalocyanine ground-state absorption. This corroborates the efficient transfer of singlet-excited-state energy from the subphthalocyanine (2.12 eV) to the fullerene moiety (1.76 eV).[10] A quantitatively similar picture was gathered in a polar environment such as benzonitrile.

To complement the emission studies, time-resolved transient absorption measurements were conducted with dyads **1a−c** in toluene and compared to those of the corresponding references **3** and **5**, following 532 nm laser excitation. In reference **3**, the singlet−singlet features of the subphthalocyanine moiety ($\lambda_{\max} = 650$ nm, $\lambda_{\min} = 570$ nm) decay with an intramolecular rate of $1.7 \times 10^{9}\ \mathrm{s}^{-1}$ to generate the triplet manifold ($\lambda_{\max} = 460$ and 620 nm, $\lambda_{\min} = 570$ nm). The latter features are reliable attributes of the subphthalocyanine triplet excited state. A heavy atom effect, due to the presence of iodo substituents, is believed to be responsible for the acceleration of the intersystem crossing.

In sharp contrast to reference **3**, dyads **1a−c** give rise to an ultrafast deactivation ($2 \pm 1 \times 10^{10}\ \mathrm{s}^{-1}$) of the subphthalocyanine singlet excited-state maxima. In particular, simultaneous to the rapid decay around 650 nm, the fullerene singlet−singlet features grow in around 880 nm, revealing identical dynamics. In fullerene reference **5**, intersystem crossing ($5.0 \times 10^{8}\ \mathrm{s}^{-1}$) due to the energetically lower-lying fullerene triplet dominates the deactivation of the singlet excited state. Interestingly, in dyads **1a−c**, the 880 nm transition (product of the initial transfer of singlet excited-state energy) decays slightly with kinetics, which are barely faster ($\sim 8.0 \times 10^{8}\ \mathrm{s}^{-1}$).

In summary, with a novel series of SubPc−C_{60} ensembles, we have demonstrated that a singlet−singlet energy transfer dominates over an intramolecular electron transfer. This observation is in good agreement with the thermodynamics of the investigated systems that predict a highly exergonic energy transfer ($-\Delta G° \sim 0.36$ eV) and a less exergonic electron transfer reaction ($-\Delta G° \sim 0.29$ eV). A more detailed study of the electrochemical and photophysical properties of this new kind of compounds will be reported in due course, especially to shed light on the apparent controversy between electrochemically and photochemically determined interactions.

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[10] Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695−703.