COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Charge-transfer states in strongly coupled phthalocyanine fullerene ensembles†

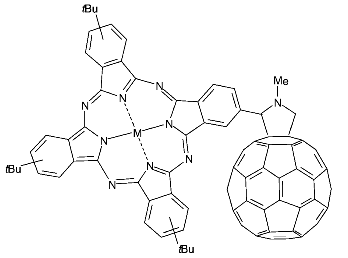
Dirk M. Guldi,*[a] Andreas Gouloumis,[b] Purificación Vázquez[b] and Tomás Torres*[b]
[a] *Radiation Laboratory, University of Notre Dame, IN, 46556, USA. E-mail: guldi.1@nd.edu*
[b] *Departamento de Química Orgánica (C-I), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. E-mail: tomas.torres@uam.es*

Received (in Cambridge, UK) 10th June 2002, Accepted 29th July 2002
First published as an Advance Article on the web 15th August 2002

Fluorescence and transient absorption measurements show that in strongly coupled ZnPc-C_{60} and H_2Pc-C_{60} dyads charge-separated states are formed; large $-\Delta G_{CR}°$ and small λ assist in stabilising ZnPc$^{\cdot+}$-$C_{60}^{\cdot-}$/H_2Pc$^{\cdot+}$-$C_{60}^{\cdot-}$.

Phthalocyanines (**Pc**) and related analogues[1] have drawn considerable attention as new molecular materials that give rise to outstanding electronic and optical properties.[2] Owing to the unique redox- and photochemical features of **Pc**s, the design of **Pc-C_{60}** systems appears particularly promising. These kind of systems were prepared first by Hanack and Hirsch,[3] who carried out spectroelectrochemical investigations; charge transfer from **Pc** to **C_{60}** was, however, ruled out under ambient conditions. To the best of our knowledge, photoinduced energy/electron transfer events have never been studied in covalently linked **Pc-C_{60}** dyads. In this work we report on photoinduced charge-separation in **ZnPc-C_{60}** and **H_2Pc-C_{60}** ensembles.

The electronic absorption spectrum of **ZnPc-C_{60}**‡ features the transitions of **ZnPc** and **C_{60}**. Specifically, maxima in the visible at 348, 614 and 681 nm correspond to those of the **ZnPc** subunit, while the **C_{60}** moiety transitions are observed in the UV at 265 and 330 nm. Nonetheless, comparing the Q-band of **ZnPc-C_{60}** to that of the (tetra-*tert*-butylphthalocyaninato-)zinc(II) (**ZnPc**) used as a reference, red-shifts (*i.e.*, 681 nm → 683 nm) and lower absorption coefficients are noted.§ These trends suggest electronic coupling between the **ZnPc** and **C_{60}**, subunits in the dyad. In the 700–850 nm region **ZnPc-C_{60}** reveals additional, broad features (see ESI,† Fig. S1a). Subtracting the absorption of the **ZnPc** and **C_{60}** references from those of the **ZnPc-C_{60}** dyads led to distinct peaks: for instance in chloroform we found a maximum at 740 nm (see ESI,† Fig. S1b). None of the references exhibit this feature and, thus, we assign this additional band to a charge-transfer transition, for which we determined absorption coefficients of 8375 and 2250 M^{-1} cm^{-1} in chloroform and *o*-dichlorobenzene, respectively. With the features of the charge-transfer absorption in hand, the electronic coupling elements (V) were estimated in chloroform as 525 cm^{-1} and in *o*-dichlorobenzene as 298 cm^{-1}.[5]



ZnPc-C_{60} (M = Zn) and **H_2Pc-C_{60}** (M = H_2).

The **ZnPc** fluorescence shows a quantum yield of 0.3 in toluene and a maximum at 690 nm. Relative to this we found the fluorescence of the **ZnPc-C_{60}** dyad red-shifted to 698 nm and its quantum yield reduced (toluene: 0.009). In polar solvents the quantum yields are further decreased and reach values as low as 0.0055—see Table 1. From the solvent dependence we infer an efficient electron transfer quenching of the locally excited **ZnPc** chromophore. Further support for this argument comes from the energy gap ($-\Delta G_{CS}°$), associated with charge-separation, as a function of solvent polarity (ε). The energies of the charge-separated state (1.01–1.4 eV) lie notably below those of the two singlet excited states, that is, **^{1*}ZnPc** (1.79 eV) and **$^{1*}C_{60}$** (1.76 eV),[6] which suggests a strongly exothermic electron transfer in both instances to form **ZnPc$^{\cdot+}$-$C_{60}^{\cdot-}$**. A closer inspection of the emission spectra reveals a substantial broadening. Although fullerenes typically fluoresce in the range of the spectral broadening, these contributions can be ruled out, bearing in mind the low yields (Φ = 6.0 × 10^{-4}).[6] In line with the assumption that the width of the charge-transfer emission relates to $(4\lambda_S k_B T)^{1/2}$, lowering the temperature to 77 K helped to convolute the emission bands, which are broad at room

Table 1 Photophysical and thermodynamic properties of **ZnPc-C_{60}**

		ZnPc-C_{60}			
	ZnPc	Toluene	Chloroform	*o*-Dichlorobenzene	Benzonitrile
Φ (fluorescence)	0.3	0.009	0.0073	0.0066	0.0055
τ_{CT} (fluorescence)/ns		3.6	3.05	2.7	2.3
τ_{CT} (transient absorption)/ns		3.1	3.0	not stable	2.29
λ_{max} (CT absorption)/nm		Masked by the Q-band	740	772	Not detectable
λ_{max} (CT emission)/nm		770	777	809	821
V/cm^{-1}			525[a]	298[b]	301[b]
$\Delta G_S{}^c$/eV		0.14	0.04	0	−0.25
$-\Delta G_{CS}{}^{°c}$/eV		0.39	0.49	0.53	0.78
$-\Delta G_{CR}{}^{°c}$/eV		1.4	1.3	1.26	1.01
λ_S/eV		0.2	0.29	0.27	0.49
λ_i/eV			0.04	0.04	
λ/eV			0.33	0.31	

[a] R_{CC} = 10.8 Å; ε = 8375 M^{-1} cm^{-1}; ν = 13514 cm^{-1}; $\Delta\nu_{1/2}$ = 648 cm^{-1}. For details see ref. 5. [b] R_{CC} = 10.8 Å; ε = 2250 M^{-1} cm^{-1}; ν = 12953 cm^{-1}; $\Delta\nu_{1/2}$ = 840 cm^{-1}. For details see ref. 5. [c] Determined with the dielectric continuum model and the following parameters: R_+ = 6.65 Å; R_- = 3.6 Å; R_{CC} = 10.8 Å; $E_{1/2}$ ($D^{\cdot+}$/D) = 601 mV; $E_{1/2}$ (A/$A^{\cdot-}$) = −660 mV.[4b] See for details: F. Hauke, A. Hirsch, S. G. Liu, L. Echegoyen, A. Swartz, C. Luo and D. M. Guldi, *Chem. Phys. Chem.*, 2002, **3**, 195.

---

† Electronic supplementary information (ESI) available: UV-Visible spectra and charge-transfer for features of **ZnPc-C_{60}** and **ZnPc**. See http://www.rsc.org/suppdata/cc/b2/b205620h/

DOI: 10.1039/b205620h

temperature. The detection of the charge transfer emission is not limited to toluene, even using polar media leads to similar features. An illustrative example is given in Fig. 1, which shows a maximum at 809 nm for the *o*-dichlorobenzene case, together with the fluorescence spectra of a suitable C$_{60}$ reference.

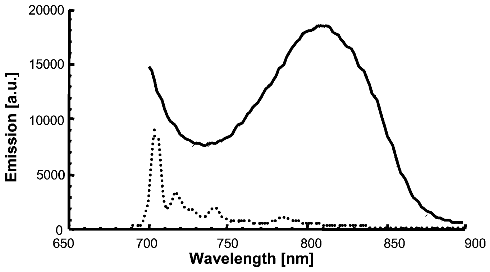


Fig. 1 Fluorescence spectra of **ZnPc-C$_{60}$** (solid line) in *o*-dichlorobenzene and **C$_{60}$** reference (dotted line) at 77 K with matching absorption at the 670 nm excitation wavelength.

The energy difference between absorption and emission is small: The values are 0.08 eV (chloroform) and 0.075 eV (*o*-dichlorobenzene). Considering that the energetic differences nearly equal $2\lambda_V$,[7,8] we can estimate the reorganisation energy (λ_V) to 0.04 ± 0.01 eV in both solvents. This suggests that any influence of the solvent on the charge transfer parameters relates to changes in the outer-sphere reorganisation energy.[8] Evidence for this hypothesis comes from the following observation: the position of the charge-transfer band is given by $-(\lambda_S + \Delta G_{CR}°)$ as the transition takes place down to the lowest vibrational level of the singlet ground state. λ_S-Values of 0.32 ± 0.01 eV result for **ZnPc-C$_{60}$** in chloroform and also in *o*-dichlorobenzene.

To shed light onto the fate of the photoexcited **^{1*}ZnPc**, solutions of **ZnPc-C$_{60}$** were probed by time-resolved fluorescence decay measurements and compared with those of the **ZnPc** reference. In **ZnPc-C$_{60}$** the emission lifetime fit to a first order rate law with values ranging between 2.3 and 3.6 ns (Table 1).¶ Taken all the results into concert, we conclude that the origin of the long-lived emission in **ZnPc-C$_{60}$** is a low-lying charge-transfer state.

To probe the mechanism by which the **ZnPc** subunit singlet excited state in **ZnPc-C$_{60}$** is deactivated, transient absorption changes were recorded with several time delays after a short picosecond laser pulse. At early times (*i.e.* 20 ps), they are practically identical to those of the **ZnPc** reference, exhibiting a singlet–singlet absorption around 825 nm (see NIR part in Fig. 2). Instead of the slow ISC dynamics (3.0×10^8 s^{-1}), the lifetime of the singlet excited state is governed by a prompt and rapid intramolecular decay of the singlet–singlet transition. The transient absorption changes, recorded at the conclusion of the fast deactivation (see Fig. 2) show a sharp peak around 860 nm, the characteristic near-IR fingerprint of the one-electron oxidised **ZnPc$^{\cdot+}$**. This peak is accompanied by a maximum in the visible, at 550 nm. As far as the C$_{60}$ moiety is concerned, a transient maximum in the near-infrared around 1000 nm corroborates the reduction of the acceptor.[6]

The decay curves of both fingerprints, that is, **ZnPc$^{\cdot+}$** and **C$_{60}$$^{\cdot-}$** fit closely to a single exponential decay. More importantly, the lifetimes of a few nanoseconds resemble those seen for the charge-transfer emission—see Table 1. The dependence of k_{CR} *vs.* free energy changes indicates stabilising effects for the charge-separated state at higher $-\Delta G_{CR}°$ values. These are clear attributes describing the inverted region of the classical Marcus-parabola.[9] To further enlarge the energy gap ($-\Delta G_{CR}°$) we probed the corresponding metal free **H$_2$Pc-C$_{60}$** dyad.† Removal of the metal center shifts the one-electron oxidation of the phthalocyanine macrocycle by ~0.13 V to more anodic potentials and thereby increases $-\Delta G_{CR}°$.[4] In fact, the lifetime of the charge-separated state (**H$_2$Pc$^{\cdot+}$-C$_{60}$$^{\cdot-}$**),‖ as determined from fluorescence and transient absorption measurements vary now between 3.9 ns (benzonitrile), 5.1 ns (*o*-dichlorobenzene) and 5.5 ns (chloroform). These values are appreciably larger than what is seen for **ZnPc$^{\cdot+}$-C$_{60}$$^{\cdot-}$**

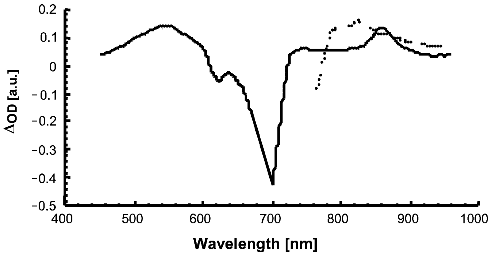


Fig. 2 Differential absorption changes recorded 50 ps after photo-excitation of **ZnPc** (dashed spectrum) and **ZnPc-C$_{60}$** (solid spectrum) in deoxygenated toluene (~1.0×10^{-5} M); excitation of ZnPC with 355 nm.

Unmistakably, the slower decay rates benefit from the larger driving forces [**H$_2$Pc-C$_{60}$**: $-\Delta G_{CR}° = (+1.53) - (+1.14)$ eV; **ZnPc-C$_{60}$**: $-\Delta G_{CR}° = (+1.40) - (+1.01)$ eV]. Another important incentive evolves from the solvent reorganisation energy. Comparing **H$_2$Pc-C$_{60}$** and **ZnPc-C$_{60}$**, smaller λ_S-values are determined from the charge-transfer emission for the free-base dyad; toluene (0.03 eV), chloroform (0.14 eV), *o*-dichlorobenzene (0.16 eV) and benzonitrile (0.38 eV). Since R_{CC}, as the only other sensitive variable in control over λ, remains the same in the two different dyads, structural parameters must be taken into account. For example, partial charge localisation at the zinc metal in **ZnPc$^{\cdot+}$-C$_{60}$$^{\cdot-}$** is likely to attenuate λ_S. This guarantees only in **H$_2$Pc$^{\cdot+}$** a homogeneous delocalisation of the charge over the π-system.

In summary, extending previous work by Imahori *et al.*[8] our current work succeeds in the determination of λ_S- and λ_V-values for C$_{60}$-based dyads in polar solvents. Therefore, the values (λ = 0.32 ± 0.01 eV; **ZnPc-C$_{60}$** and λ = 0.19 ± 0.01 eV; **H$_2$Pc-C$_{60}$**) emerge as realistic reference points for λ in C$_{60}$-based systems.

This work was supported by the Office of Basic Energy Sciences of the US Department of Energy (NDRL-4401), CICYT (MAT-99-0180) and the Comunidad de Madrid (07N/0051/2001).

Notes and references

‡ **ZnPc-C$_{60}$** and **H$_2$Pc-C$_{60}$** were synthesized by reaction of C$_{60}$ with the corresponding tri-*tert*-butylformylphthalocyanine in the presence of an excess of *N*-methylglycine in *ca.* 70% yield, based on recovered C$_{60}$.[4b]

§ The changes in the UV-visible spectrum upon substitution of the Pc by C$_{60}$, cannot be attributed to aggregation, since the spectrum is not affected by using different concentrations (10^{-5}–10^{-6} M).

¶ For **ZnPc** reference a mono-exponential decay was found, yielding a fluorescence lifetime of 3.8 ns. To rule out intermolecular effects, a concentration dependence (3.5–65 μM) of the fluorescence features was run and quantum yield/lifetime are virtually constant.

‖ **H$_2$Pc$^{\cdot+}$** shows a transient maximum at 915 nm.

1 *Phthalocyanines: Properties and Appl., Vols. 1-4*, ed. C.C. Leznoff and A.B. Lever, VCH, Weinheim, 1989, 1993, 1996; C. G. Claessens, D. González-Rodríguez and T. Torres, *Chem. Rev.*, 2002, **102**, 835.
2 G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *J. Mater. Chem.*, 1988, **8**, 1671.
3 (*a*) T. G. Linssen, K. Dürr, M. Hanack and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1995, 103.
4 (*a*) Á. Sastre, A. Gouloumis P. Vázquez, T. Torres, V. Doan, B. J. Schwartz, F. Wudl, L. Echegoyen and J. Rivera, *Org. Lett.*, 1999, **1**, 1807; (*b*) A. Gouloumis S.-G. Liu, Á. Sastre, P. Vázquez, L. Echegoyen and T. Torres, *Chem. Eur., J.*, 2000, **6**, 3600.
5 N. Armaroli, G. Marconi, L. Echegoyen, J.-P. Bourgeois and F. Diederich, *Chem. Eur., J.*, 2000, **6**, 1629.
6 (*a*) D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.
7 (*a*) H. Oevering, M. N. Paddon-Row, M. Heppner, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258; (*b*) R. A. Marcus, *J. Phys. Chem.*, 1989, **93**, 3078.
8 H. Imahori, N. V. Tkachenko, V. Vehmanen, K. Tamaki, H. Lemmetyinen, Y. Sakata and S. Fukuzumi, *J. Phys. Chem. A*, 2001, **105**, 1750.
9 R. A. Marcus, *Angew. Chem., Int. Ed.*, 1993, **32**, 11.