Chemical Science

EDGE ARTICLE

Cite this: Chem. Sci., 2013, 4, 1338

Received 10th November 2012 Accepted 14th January 2013

DOI: 10.1039/c3sc21956a

www.rsc.org/chemicalscience

Introduction

Fullerenes and fullerene derivatives are being widely used as active components in optoelectronic devices such as photovoltaic cells due to their outstanding photophysical and electrochemical properties.1 Much effort has been devoted to the understanding of the interactions between fullerenes and other chromophores, which coexist within these devices in order to improve their performances.² One possible approach towards a better understanding of the morphology of fullerene-based devices is to study their interactions with supramolecular receptors which, moreover, are also chromophoric species. The design of new receptors for fullerenes is based on three principles: (i) shape complementarity or optimization of the interacting surface, (ii) electrostatic complementarity with the electron deficient fullerene, and (iii) entropic factors such as the hydrophobic effect.³ Past experiments have documented that maximization of π - π stacking interactions is a desirable feature in the design of fullerene receptors, especially to fine-tune recognition. In principle, flat aromatic surfaces might be unsuitable as receptors for convex fullerenes. Still, many planar

I. Sánchez-Molina,^a C. G. Claessens,^{*a} B. Grimm,^b D. M. Guldi^{*b} and T. Torres^{*ac}

Six electronically different concave-shaped subphthalocyanines (SubPcs) have been prepared for testing the structural factors governing fullerenes encapsulation. Thus, the supramolecular interaction of SubPcs with C_{60} and C_{70} fullerenes in solution has been studied by Job's plot and titration experiments, which yielded quantitative information on both the stoichiometry and strength of the complexes in toluene solution. The importance of the electronic nature of the SubPc was demonstrated, as it influences not only the stability of the complex, but also its stoichiometry. Alkyl chains incorporated in hexaalkylthio-substituted SubPcs seem to in some way cooperate in the binding process and influence its kinetics. In the resulting 2 : 1 complexes, the large absorption cross section of SubPcs throughout the visible part of the spectrum is the beginning of an unidirectional energy transfer to funnel the excited state energy from the periphery (*i.e.*, two SubPcs) to the core (*i.e.*, C_{60} and C_{70}).

chromophores, including porphyrins, *etc.*, have been shown to interact favourably with fullerenes. Moreover, remarkable results have been realized in the area of porphyrin-based receptors,^{3g} owing to the preorganization of the host. The strategy of preorganization is very powerful, especially in the context of enhancing fullerene encapsulation. A convenient alternative to the aforementioned is the use of aromatic receptors, like, for example, SubPcs, which feature adequate and complementary shapes to fullerenes.

Subphthalocyanines (SubPcs) are 14 π -electron macrocycles composed of three 1,3-diiminoisoindole units N-fused around a central boron atom (Fig. 1). Their synthetic versatility and their attractive physical properties have given rise to interesting applications in the fields of nonlinear optics and organic photovoltaics.⁴ Their C₃ symmetric bowl-shaped structure is apparently perfectly adapted, at least from a geometric point of view, to the convex surface of fullerenes. Formation of a 1:1 complex of a SubPc with C60 fullerene in solution has been previously mentioned by Ziessel et al.5 even if no quantitative data were reported. In the solid state, Kobayashi et al.6 described the 1:1 complex between fullerene and a π -extended subphthalocyanine. Incorporation of C₆₀ fullerene within a homodimeric metallosupramolecular subphthalocyanine capsule was also demonstrated. Nevertheless, in this case, no quantitative data were reported since C60 was extracted from acetone, a solvent in which it is barely soluble.7 Interestingly, there are also many reports dealing with the photoinduced electron and energy transfer between C₆₀ and SubPc units within covalent dyads. These studies have shown that the communication between the components is highly dependent on the distance, which separates them and the nature of the peripheral substituents on the SubPc moiety.8 However, and to the extent of our knowledge, this

1338 | Chem. Sci., 2013, 4, 1338-1344

View Article Online

^aDepartamento de Química Orgánica (C-1) Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. E-mail: tomas.torres@uam.es; Fax: +34 913 973 966; Tel: +34 914 0974 151

^bFriedrich-Alexander-Universität Erlangen-Nürnberg, Institute for Physical Chemistry, Egerlandstr. 3, D-91058 Erlangen, Germany. Fax: +49 9131-852-8307

^cIMDEA-Nanociencia, Ciudad Universitaria de Cantoblanco, c/ Faraday, 9, 28049 Madrid, Spain

[†] Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data. NMR, MS and IR spectra for all novel compounds. Fluorescence spectra, steady state and transient absorption spectra. See DOI: 10.1039/c3sc21956a

Trapping fullerenes with jellyfish-like subphthalocyanines†

Another motivation to address a good understanding of the interaction of these molecules, was the thought that it might help in the elucidation of their interaction at the interface between two layers, which is also crucial for device optimization. Evaporated organic solar cells in which the two active layers were subphthalocyanine and C_{60} were shown to display high efficiencies, up to 3.6%.⁹

Thus, from these preliminary studies it is clear that there is a strong need for clarifying and quantifying the nature and scope of the supramolecular interactions between SubPcs and fullerenes. In order to do so we describe in this article the synthesis of a series of acceptor, neutral and donor subphthalocyanines and the careful study of their complexing ability towards C_{60} and C_{70} fullerenes in solution. In the first instance we expect to control the intensity of the interaction with fullerene through the modification of the electronic nature of the SubPc macrocycle.

Thus, we chose dodecafluorosubphthalocyanine **1b** as acceptor, unsubstituted SubPc **2b** as neutral, and hexathioether SubPcs **3–6b** as donor components.

Furthermore, the donor SubPcs possess alkyl chains which may strengthen the complexation of C₆₀ and C₇₀ fullerenes through additional van der Waals interactions. One motivation for designing new fullerene receptors was built around entropic factors that would fine tune hydrophobic effects. To this end, the alkyl chains of the hexaalkylthio-substituted SubPcs are expected to mutually interact and, thereby, to facilitate/ augment the encapsulation of fullerenes. As a matter of fact, fine-tuning/optimizing these factors is supposed to impact the kinetics of SubPc-fullerene excited state interactions. To corroborate the aforementioned hypotheses, a series of alkylthio-substituted SubPcs was synthesized and investigated with particular emphasis on the encapsulation of fullerenes by means of photophysical assays. Thus, four different SubPcs 3-6 with increasing chain-length (C2, C4, C8 and C16, respectively) were synthesized with the aim of determining the role and importance of these moieties in the formation of the complexes.



Fig. 2 Absorption spectra of 1b (grey), 2b (black) and 6b (red).

Results and discussion

Synthesis

Subphthalocyanines **1b–6b** were synthesized following a two-step one-pot reaction previously developed in our research group.¹⁰ Accordingly, the corresponding phthalonitriles (tetra-fluorophthalonitrile for **1b**, phthalonitrile for **2b** and 4,5-dia-lkylthiophthlontrile for **3b–6b**) were cyclotrimerized in the presence of boron trichloride to yield SubPcs **1a–6a** which, after evaporation of *p*-xylene, were further treated in the same reaction vessel with *tert*-butyl phenol in toluene at reflux temperature. Final compounds **3b–6b** were purified by column chromatography on silica gel and were obtained in moderate to good yields (from 40% to 70%). It is worth mentioning that all the reactions have been optimized and, more relevantly, scaled up to gram quantities without appreciable loss of efficiency. All new compounds were characterized by ¹H-NMR, ¹³C-NMR spectroscopy, UV-vis spectrophotometry as well as mass spectrometry.

MALDI-TOF mass spectra of compounds **1b–6b** show peaks at 760.14, 544.24, 904.26, 1072.42, 1408.64, 2082.36, respectively, corresponding to $[M]^+$. In the case of thioether-substituted SubPcs **3b–6b** prominent peaks corresponding to the loss of the axial *tert*-butylphenoxy group were observed. These observations confirm the higher liability of the axial



Fig. 1 Synthesis of subphthalocyanines 1-6.



Fig. 3 Representation of the Job's plots for the complex formation of 1-6b with C_{60} (from left to right and top to bottom).

ligands observed experimentally when the macrocycle is peripherally substituted with donor groups. Actually, the axial substitution reaction is complete for thioether SubPcs within 2 hours, in contrast with dodecafluoro and dodecahydro SubPcs, which require 18–24 h. Hence, mass spectrometry results are in good agreement with the reactivity observed in the macrocycles.

UV-vis spectra of SubPcs **1b–6b** show the expected B and Q bands at *ca.* 320 and *ca.* 580 nm, respectively. In the case of donor subphthalocyanines **3b–6b**, the Q band is bathochromically shifted from 570 to 605 nm (Fig. 2). It is worth mentioning the presence of a weak absorption band at *ca.* 400 nm in compounds **3b–6b** which is most probably due to an $n-\pi^*$ transition between the lone pair of the sulphur atoms and the adjacent aromatic ring.

Host-guest behaviour

The complexing ability of SubPcs **1b–6b** towards C_{60} and C_{70} fullerenes was demonstrated through an extensive series of Job's plots and titration experiments; all of them performed in toluene and employing the UV-visible spectrophotometry technique. Notably, extensive elaborations about the impact of the solvent on the complex formation have not been carried out. However, in the initial phase of our experiments we checked the interactions between SubPcs and fullerenes in acetone and chloroform by

means of ESI-mass experiments. In both cases, the formation of SubPc-fullerene complexes evolved with 1 : 1, 2 : 1, and in some cases with 3 : 1 stoichiometries. Perfluorinated subphthalocyanine **1b** and C₆₀ or C₇₀ were not expected to interact because their electronic nature is not complementary (both compounds are electronically deficient); Job's plot experiments carried out in toluene confirmed our hypothesis, as illustrated in Fig. 3 and S1.[†] These results indicate that shape complementarity alone is not enough for SubPcs to interact appreciably with fullerenes. In the case of unsubstituted subphthalocyanine **2b**, a 1 : 1 complex with either C₆₀ or C₇₀ was shown to form in toluene with a clear maximum at 0.5 mole fraction (Fig. 3 and S1[†]).

More strikingly, the introduction of six donor thioalkyl chains in the periphery of the macrocycles (3b-6b) gave rise to the formation of 2 : 1 complexes. Here, two SubPcs encapsulate one fullerene. The length of the alkyl chain influences dramatically the time required for the binding process to reach equilibrium. For example, the latter occurred immediately for lipophilic SubPcs 5b and 6b, but required some time for SubPc derivatives bearing short alkyl chains, that is, 15 minutes for 4b, and around 45 minutes for 3b with C₆₀ fullerene. When studying the interactions with C₇₀, the time delay only evolved for SubPc 3b (20 minutes). One can observe that the Job's plots corresponding to the formation of the 2 : 1 complex between SubPc 3b and C₆₀ are far from perfect even after several attempts. From these



Fig. 4 Molecular modelling of the 2 : 1 adducts of SubPcs (from left to right) 3b, 4b and 5b and C₆₀.

Table 1Binding constants of SubPcs 1–6b and fullerenes C_{60} and C_{70}

| SubPc | with C_{60} (M^{-1}) | with C_{70} (M^{-1}) |
|-------|--|--|
| 1b | _ | _ |
| 2b | $\textit{K} = 2.1 \times 10^4 \pm 1.1 \times 10^3$ | $\mathit{K} = 6.6 	imes 10^2 \pm 46$ |
| 3b | $K_1 = K_2 = 2.1 	imes 10^4 \pm 2.6 	imes 10^3$ | $K_1 = K_2 = 1.9 	imes 10^4 \pm 1.9 	imes 10^3$ |
| 4b | $K_1 = K_2 = 1.9 	imes 10^5 \pm 5.2 	imes 10^4$ | $K_1 = K_2 = 1.1 	imes 10^4 \pm 2.2 	imes 10^3$ |
| 5b | $K_1 = K_2 = 2.9 	imes 10^4 \pm 1.1 	imes 10^3$ | $\textit{K}_{1} = \textit{K}_{2} = 1.3 \times 10^{4} \pm 3.6 \times 10^{3}$ |
| 6b | $K_1 = K_2 = 4.4 	imes 10^4 \pm 2.6 	imes 10^3$ | $K_1 = 3.6 	imes 10^5 \pm 2.7 	imes 10^4, K_2 = 1.8 	imes 10^5 \pm 3.8 	imes 10^4$ |



Fig. 5 Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (540 nm) of **5b** (2.5×10^{-5} M) in toluene with several time delays between 0 and 2800 ps at room temperature – see figure legend for details. Lower part – time absorption profiles of the spectra at 675 (black spectrum), 860 (orange spectrum) and 1250 nm (red spectrum), monitoring the excited state dynamics.

experimental observations we infer that the alkyl chains have a structuring role in the formation of the complexes with fullerenes. In Fig. 4, representation of the molecular structure of the 2:1 complexes between SubPcs **3b**, **4b** and **5b** and C₆₀ confirms the necessary interactions between the alkyl chains when the number of carbon atoms of the alkyl chains exceeds 4.

To obtain a quantitative understanding of the interactions between SubPcs and fullerenes, binding constants for all of the previously described complexes were derived from titration experiments monitored by UV-visible spectroscopy. The only



Fig. 6 Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (540 nm) of **5b** (2.5×10^{-5} M) and C₇₀ in toluene with several time delays between 0.1 and 2800 ps at room temperature – see figure legend for details. Lower part – time absorption profiles of the spectra at 675 (black spectrum) and 1250 nm (red spectrum), monitoring the excited state dynamics.

notable exception is **2b**, whose binding constants with C_{60} and C_{70} were obtained from the Job's plots (Fig. 3 and S1[†]).

At first glance, no changes appear in the spectra during the titration. However, the spectra differ from the sum of the individual spectra, that is, SubPc and C_{60} . This difference of absorbance around 360 nm was plotted *versus* increasing concentrations of SubPcs, and curve fitting afforded the values of the binding constants (Table 1). It is worth mentioning that, despite evidence for a 2 : 1 stoichiometry in the Job's plots of **3b**–**6b** with C_{60} and C_{70} , the shape of the titration curves corresponds to the typical absorbance hyperbola for 1 : 1 complexes. On one



Fig. 7 Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (540 nm) of **5b** (2.5×10^{-5} M) and C₆₀ in toluene with several time delays between 0.1 and 2800 ps at room temperature – see figure legend for details. Lower part – time absorption profiles of the spectra at 675 (black spectrum) and 1250 nm (red spectrum), monitoring the excited state dynamics.

hand, this fact may be rationalized on the basis of a 1:1 complex, if the charge transfer occurs only from one of the two SubPcs. On the other hand, the stepwise formation of a 2:1 complex, where both binding constants have the same value, cannot be ruled out. The former interpretation was, however, discarded, since, if true, should be reflected in the Job's plot experiments. As a matter of fact, the latter interpretation was used for the curve fitting. The titration of C_{70} with SubPc **6b** (C16 alkyl chains) gave rise to a typical sigmoidal curve, from which different K_1 and K_2 values were derived – see ESI.[†]

Overall, the binding constants are quite high, with values ranging from 10^4 to 10^5 M⁻¹ and, as such, attest the strong interactions between SubPcs and fullerenes. In spite of the different kinetic behaviour in terms of complex formation – *vide supra* – no general trend in binding constants is noted. In fact, the differences between the binding constants are insignificant and, in turn, hamper the drawing of any meaningful conclusion.

Photophysics

Further insights into the interactions between SubPcs and C_{70} as well as between SubPcs and C_{60} came from femtosecond resolved

pump probe experiments. SubPcs **4**, **5** and **6b** were selected for the study and all of them showed a very similar behaviour. Common to all of the SubPcs is that photoexcitation at, for example, 540 nm generates a singlet excited state, whose characteristics involve minima at around 600 nm accompanied by maxima at 485, 680, and 870 nm. An example is shown in Fig. 5. With a lifetime of 1250 ± 50 ps these singlet excited states transform into the corresponding triplet excited states. The latter feature minima at 600 nm as well as maxima at 490, 645, and 865 nm.

It is important to note that Fig. 6 and 7 attest that the SubPcs singlet excited state characteristics evolve despite the presence of C_{60} and/or C_{70} . Nevertheless, in the presence of C_{70} a number of changes are discernable, especially in the near-infrared region – Fig. 6, S4 and S5.[†] Firstly, instead of the 1250 \pm 50 ps intersystem crossing dynamics, a 1240 nm maximum evolves in the case of C_{70} with a lifetime of 5.5 \pm 0.5 ps.

This and the feature at 460 nm resemble those seen in reference experiments with just C₇₀ and correlate with its singlet excited state. Secondly, no particular evidence that would corroborate the involvement of the one electron reduced form of C₇₀ is gathered. Of importance is the transient maximum at 1370 nm as registered in spectroelectrochemical or pulse radiolytical experiments.11 As a matter of fact, we conclude that energy transfer rather than electron transfer dominates the electronic interactions between SubPcs and C70 in the excited state. In line with this hypothesis is the observation that the triplet excited state of C70 with its characteristic 945 nm fingerprint evolves on the longer time scale, that is, up to 3000 ps. Moreover, this 945 nm growth - C70 triplet excited state - and the 1240 nm decay - C70 singlet excited state - mirror each other and feature the same lifetime of 1000 \pm 50 ps. Finally, the SubPc triplet-triplet maxima and the triplet-triplet minimum are noted at 490/645 and 600 nm, respectively. Their formation with 1250 \pm 50 ps matches that seen in the absence of C70 and, as such, is rationalized on the basis of free SubPcs in solution, whose singlet excited state intersystem crosses to the corresponding triplet excited state. Variation of the C₇₀ concentration, that is, either an increase or decrease, is key in terms of yielding different C70 triplet to SubPc triplet ratios, without, however, affecting the underlying energy transfer dynamics of 5.5 \pm 0.5 ps.

Less unambiguous is the situation when C₆₀ is present. The corresponding maxima of the C60 singlet excited state, especially the 960 nm fingerprint are hardly discernable - Fig. 7. Largely responsible for this trend is the fact that the corresponding SubPc transitions dominate the differential absorption changes throughout the recorded region in the visible and the near-infrared. Nevertheless, a closer analysis sheds light onto the presence of the 960 nm feature. It was identified in the form of a shoulder. The presence of C₆₀, like that of C₇₀, evokes a rapid decay, namely 4.5 ± 0.5 ps, of the SubPc singlet excited state. Taken the aforementioned into concert, an energy transfer scenario is operative upon SubPc-C₆₀ complex formation. The one electron reduced form of C₆₀, on the other hand, is not seen at 1080 nm even on longer time scales of up to 3000 ps. Instead, the formation of the C₆₀ triplet excited state at 750 nm is noted as a consequence of an efficient intersystem crossing.

Conclusions

A systematic and quantitative study of the supramolecular interaction of SubPcs with fullerenes in solution has been carried out. Systematic variations of the peripheral substitution of SubPcs assist in the control over the non-covalent forces at work. To this end, hydrophobic interactions complemented by π - π interactions are the major driving forces behind a 2:1 complexation between two hexaalkylthioSubPcs and one C60 (or C_{70}), with binding constants as large as 10^5 M^{-1} . In the resulting 2:1 inclusion complexes, an unidirectional energy transfer from the periphery (*i.e.*, two SubPcs) to the core (*i.e.*, C_{60} and C₇₀) has been determined to occur upon photoexcitation. At the current stage of our research, it is hard to make serious predictions about the applicability of our binding motif towards improving organic photovoltaics. Despite the lack of electron transfer in our solution based experiments, such events are, nevertheless, expected in organic photovoltaic devices. On this connection, we like to draw attention to previous results with acceptor perfluorinated SubPcs.96 Moreover, deaggregation of fullerenes by the chromophore might be a useful approach for achieving better architectures in bulk-heterojunction solar cells.

Experimental

Synthesis

General method for the synthesis of 4,5-dialkylthiophthalonitriles:¹² 4,5-dichlorophthalonitrile (1 g, 5.08 mmol), K_2CO_3 (2.1 g, 15.24 mmol) and degassed *N*,*N*-dimethylacetamide (13 ml) were placed in a round bottomed flask under argon atmosphere. The corresponding thiol (12 mmol) was added and the mixture was stirred at 90 °C for 12 h. Characteristics of **2c** and **d** are identical to those previously described.

General method for the synthesis of subphthalocyanines 1-6b: in a 25 ml round bottomed flask, BCl₃ (0.3 mmol, 1 M solution in *p*-xylene) was added to the corresponding phthalonitrile (0.6 mmol) under an argon atmosphere. The reaction mixture was stirred under reflux for 2 h and then flushed with argon to remove volatiles. Subsequent axial substitution was carried out without isolation of chlorosubphthalocyanines intermediate. 4-tertbuthylphenol (1.8 mmol) and toluene (1 ml) were added and the mixture was refluxed till reaction was completed (check by TLC; see eluent below). Reaction was cooled down to room temperature, the solvent was evaporated under reduced pressure and the resulting purple-green solid was washed with a 4 : 1 mixture of methanol and water. Finally, compounds 1-6b were purified by column chromatography in silica gel using as eluent: hexanetoluene (1:2.5) for 3 and 4b, hexane-CH2Cl2 (1:1) for 5b, hexane-ethyl acetate (20:1) for 6b, toluene-THF (20:1) for 2b and hexane-CHCl3 (2:1) for 1b. Characteristics of compounds 1c-f are identical to those previously described.12b,13

Acknowledgements

Support is acknowledged from the Spanish MEC (CTQ2011-24187/BQU and CONSOLIDER INGENIO 2010, CSD2007-00010 on Molecular Nanoscience), MICINN (PRI-PIBUS-2011-1128),

the Comunidad de Madrid (MADRISOLAR-2, S2009/PPQ/1533), the EU (FP7- ICT-2011.3.6, Nr: 287818), Fonds der Chemischen Industrie (FCI) and Deutsche Forschungsgemeinschaft (SFB 583), and Free State of Bavaria (Solar Technologies go Hybrid).

Notes and references

- 1 (a) Fullerenes, ed. A. Hirsch and M. Brettreich, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005; (b)
 S. Fukuzumi and D. M. Guldi, Electron-Transfer Chemistry of Fullerenes, in Electron Transfer in Chemistry, ed. V. Balzani, Wiley-VCH Verlag GmbH, Weinheim, 2008; (c)
 R. Taylor and D. R. M. Walton, Nature, 1993, 363, 685–693; (d) M. Prato, J. Mater. Chem., 1997, 7, 1097–1109; (e)
 G. Bottari, G. de la Torre, D. M. Guldi and T. Torres, Chem. Rev., 2010, 110, 6768–6816.
- 2 (a) K. Tashiro, T. Aida, J.-Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto and K. Yamaguchi, J. Am. Chem. Soc., 1999, 121, 9477–9478; (b) K. Tashiro and T. Aida, Chem. Soc. Rev., 2007, 36, 189–197; (c) A. M. V. M. Pereira, A. R. M. Soares, A. Hausmann, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, D. M. Guldi and T. Torres, Phys. Chem. Chem. Phys., 2011, 13, 11858–11863; (d) H. Imahori and Y. Sakata, Adv. Mater., 1997, 9, 537–546; (e) P. D. W. Boyd and C. A. Reed, Acc. Chem. Res., 2005, 38, 235–242.
- 3 (a) E. M. Pérez and N. Martín, Chem. Soc. Rev., 2008, 37, 1512–1519; (b) A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau and M. M. Olmstead, J. Am. Chem. Soc., 2007, 129, 3842–3843; (c) T. Kawase and H. Kurata, Chem. Rev., 2006, 106, 5250–5273; (d) M. B. Nielsen and F. Diederich, Chem. Rev., 2005, 105, 1837–1867, and references therein; (e) E. M. Pérez, L. Sánchez, G. Fernández and N. Martín, J. Am. Chem. Soc., 2006, 128, 7172–7173; (f) T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. J. Wennerström, J. Chem. Soc., Chem. Commun., 1992, 604–606; (g) K. Tashiro and T. Aida, Chem. Soc. Rev., 2007, 36, 189–197.
- 4 (a) C. G. Claessens, D. González-Rodríguez and T. Torres, *Chem. Rev.*, 2002, **102**, 835–853; (b) A. Medina and
 C. G. Claessens, *J. Porphyrins Phthalocyanines*, 2009, **13**, 447–454; (c) T. Torres, *Angew. Chem., Int. Ed.*, 2006, **45**, 2834–2837; (d) N. Kobayashi, T. Ishizaki, K. Ishii and
 H. Konami, *J. Am. Chem. Soc.*, 1999, **121**, 9096–9110.
- 5 R. Ziessel, G. Ulrich, K. J. Elliott and A. Harriman, *Chem.–Eur. J.*, 2009, **15**, 4980–4984.
- 6 S. Shimizu, S. Nakano, T. Hosoya and N. Kobayashi, *Chem. Commun.*, 2011, 47, 316–318.
- 7 C. G. Claessens and T. Torres, *Chem. Commun.*, 2004, 1298–1299.
- 8 (a) D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz and L. Echegoyen, J. Am. Chem. Soc., 2004, 126, 6301–6313; (b) D. González-Rodríguez, E. Carbonell, G. de Miguel Rojas, C. Atienza Castellanos, D. M. Guldi and T. Torres, J. Am. Chem. Soc., 2010, 126, 6301–6313; (c) D. González-Rodríguez, E. Carbonell, D. M. Guldi and T. Torres, Angew. Chem., Int. Ed., 2009, 48, 8032–8036.

- 9 (a) H. H. P. Gommans, D. Cheyns, T. Aernouts, C. Girotto,
 J. Poortmans and P. Heremans, *Adv. Funct. Mater.*, 2007,
 17, 2653–2658; (b) H. H. P. Gommans, T. Aernouts,
 B. Verreet, P. Heremans, A. Medina, C. G. Claessens and
 T. Torres, *Adv. Funct. Mater.*, 2009, 19, 3435–3439.
- 10 (a) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux and J. Zyss, J. Am. Chem. Soc., 1998, 120, 12808–12817; (b) D. D. Díaz, H. J. Bolink, C. G. Claessens, E. Coronado and T. Torres, Tetrahedron Lett., 2007, 48, 4657–4670.
- 11 K. G. Thomas, V. Biju, D. M. Guldi, P. V. Kamat and M. V. George, J. Phys. Chem., 1999, 103, 8864.
- 12 (a) A. G. Gürek and Ö. Bekâroglü, J. Chem. Soc., Dalton Trans., 1994, 1419; (b) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux and J. Zyss, J. Am. Chem. Soc., 1998, 120, 12808.
- 13 (a) D. D. Díaz, H. J. Bolink, L. Capelli, C. G. Claessens,
 E. Coronado and T. Torres, *Tetrahedron Lett.*, 2007, 48, 4657; (b) C. G. Claessens and T. Torres, *Angew. Chem., Int. Ed.*, 2002, 41, 2561.