Subphthalocyanines

DOI: 10.1002/ange.200803131

Ethynyl–Boron Subphthalocyanines Displaying Efficient Cascade Energy Transfer and Large Stokes Shifts**

*Franck Camerel, Gilles Ulrich, Pascal Retailleau, and Raymond Ziessel**

The demand for "smart" fluorophores is ever increasing, not only for use in rapid, high-throughput procedures in biomedical analysis, but also in photodynamic cancer therapy and chemidosimetry, as well as for broader applications in electroluminescence, nonlinear optics, and laser technology. Of the many different dyes considered as fluorophores, those based on cyanine, pyrene, perylene, porphyrin, and indacene skeletons are the most promising.[1,2] As another class of potentially interesting compounds, the phthalocyanines (Pcs) and subphthalocyanines (SubPcs), a constricted form of Pcs, suffer the drawbacks of generally poor solubility and small Stokes shifts ($\Delta\lambda \approx 250\,\text{cm}^{-1}$) when excited in the low-energy absorption band.[3,4] Their solubility has, however, been enhanced by modifying the organic core with paraffin chains, which also allows these molecules to be organized at the supramolecular level in liquid crystals[5] and Langmuir–Blodgett films.[6] The subphthalocyanines, which have a boron(III) atom coordinated within the macrocycle, have been functionalized at the boron atom with alkoxy, silyloxy, and phenoxy groups,[4] and, in one instance, with a phenyl group.[7] Such species, incidentally, may be chiral when the dinitrile precursor used in the conventional syntheses does not have C_{2v} symmetry.[8]

Herein we describe a rational method for increasing both the solubility and Stokes shifts of SubPcs, and for tuning their fluorescence properties, by introducing functionalised alkynyl substituents at the boron atom. This strategy enables the addition of various functionalities without perturbing the bowl-shaped structure and the intriguing spectroscopic properties of the SubPcs. We have prepared a number of these *E*-SubPcs (*E* = ethynyl) with the objectives of enhancing solubility by introducing gallate or truxene substituents and improving their properties as fluorophores by introducing pyrene or truxene substituents, which not only increase absorption but also efficiently transfer their absorbed energy to the SubPc fluorophore. Fluorescence quenching, which potentially arises from the presence of di-*n*-butylamino units in some of the substituents used, can be switched off by the protonation of these units.

Replacement of the chlorido ligand on the boron atom in the starting material Cl-SubPc[9] is readily achieved by reaction with the corresponding Grignard reagents (ethynyltolyl **1**, ethynylphenyliodo **2**, ethynylgallate **3**, or ethynyl(di-*n*-butyl)aminophenyl **4**) in hot THF. The introduction of the iodophenyl substituent in **2** is particularly useful because of

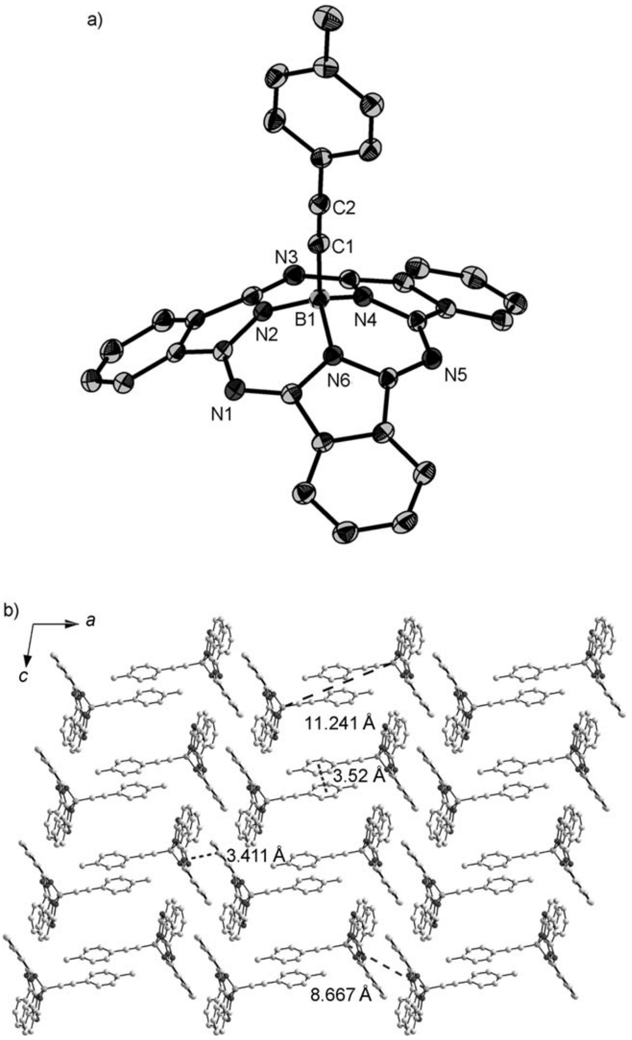


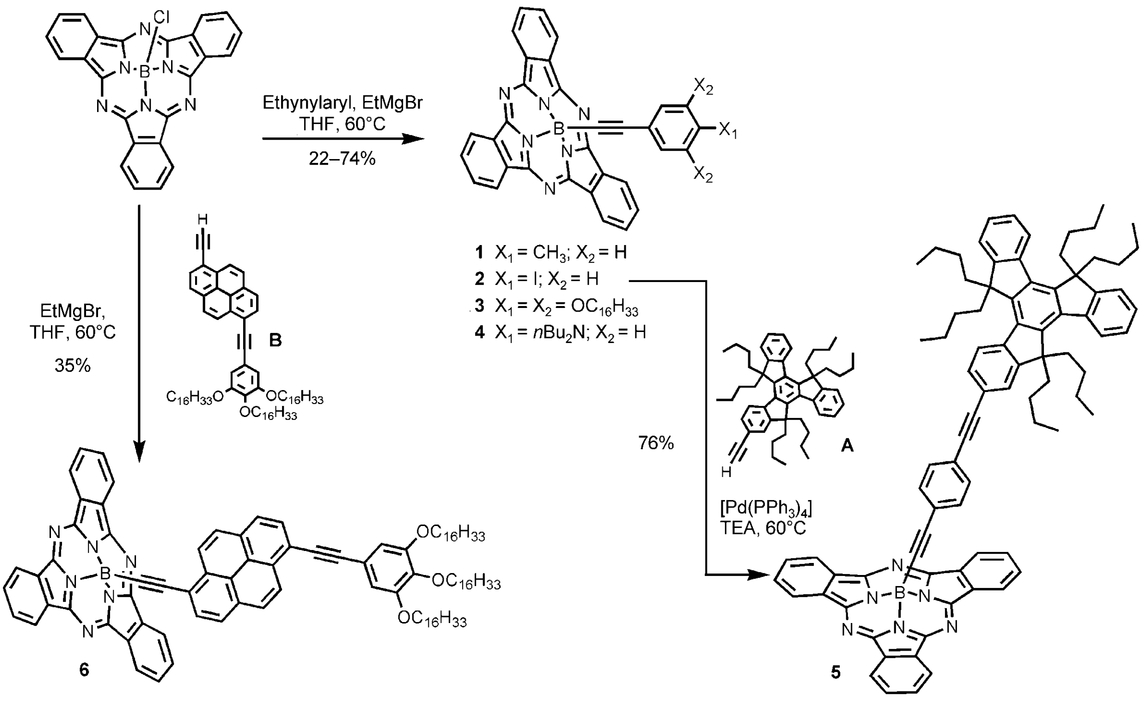
Figure 1. a) ORTEP view of compound **1** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected data B1–N2 1.504(3), B1–N4 1.499(5), B1–N6 1.502(4), B1–C1 1.586(4) Å and N2-B1-N4 103.1(2), N4-B1-N6 103.0(2), N6-B1-N2 103.4(2), N2-B1-C1 115.8(2), N4-B1-C1 115.2(2), N6-B1-C1 114.6(2)°. b) View showing the crystal packing in the *ac* plane.

---

[*] Dr. F. Camerel, Dr. G. Ulrich, Dr. R. Ziessel
Laboratoire de Chimie Moléculaire, ECPM-CNRS
25 rue Becquerel, 67087 Strasbourg Cedex 02 (France)
E-mail: ziessel@chimie.u-strasbg.fr
Dr. P. Retailleau
Laboratoire de Cristallochimie, ICSN-CNRS, Bât 27
1 avenue de la Terrasse, 91198 Gif-sur-Yvette, Cedex (France)

[**] This work was supported by the Centre National de la Recherche Scientifique and the Ministère de la Recherche et des Nouvelles Technologies. We are indebted to Prof. J. Harrowfield for his comments on the manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803131.



the ease of subsequent Pd^0-catalyzed cross-coupling reactions with ethynyltruxene (and other) derivatives in benzene/triethylamine (TEA) at 60 °C. The highly soluble *E*-SubPcs produced in all these reactions are easily purified by flash chromatography and conveniently characterized by NMR spectroscopy and mass spectrometry. The absence of aggregates is proved by the well-defined NMR spectra of these compounds. The ^{1}H NMR spectra display two multiplets in the aromatic region with a diagnostic AA′BB′ system for the isoindole core, and the ^{11}B NMR spectra show a typical singlet around −17 ppm.[4a] Although trigonal alkynylborane derivatives are well documented,[10] tetrahedral species are rare[11,12] and, to the best of our knowledge, the synthesis of *E*-SubPcs has not been reported to date.

Chloride substitution at the vertex of the boron tetrahedron by ethynyltolyl (**1**) and ethynyl(di-*n*-butyl)aminophenyl (**4**) was unambiguously confirmed by X-ray crystal structure analysis. The molecular unit discernable within the crystalline lattice of **1** shows coordination of the tetrahedral N_3C to the boron atom as well as the effective threefold symmetry of the SubPc subunit (Figure 1 a). Projection of the crystalline lattice along the *a* axis shows that the molecular array must at least in part be determined by interactions between parallel aromatic entities. In particular, in the *ac* sheet (Figure 1 b), oppositely oriented SubPc units (B–B 11.241 Å) do appear to be involved in true “face-to-face” π stacking with the formation of dimers through interactions of the tolyl rings (3.52 Å). Interestingly, the shortest B–B distance (8.667 Å) in the lattice occurs for two facing SubPc molecules located diagonally across the “voids” defined by the interlocking sheets of the view along *a*. In this centrosymmetric pair, the shortest interatomic contacts (3.411 Å) are between a bridging N atom of one SubPc unit and an aromatic C atom of the other.

The boron atom of **4** displays an almost-regular tetrahedral geometry (Figure 2 a). In contrast to **1**, a slight tilt of 12.2° between the B1–C1 and the C1–N7 axes can be observed, which shows that the ethynyl–$n\mathrm{Bu_2N}$ subunit does not bind exactly along the C_3 axis of the SubPc fragment. The lattice of compound **4** can be described as being composed of molecular layers stacked along the *c* direction. In the *ab* layer, segregation between the subphthalocyanine fragments and the ethynyl(di-*n*-butyl)aminophenyl fragments can be clearly observed. The phenyl groups weakly interact (4.24 Å) in a head-to-tail fashion to form dimers along the *a* axis whereas short contacts (3.379 Å) between the isoindole of SubPc fragments stabilize the edifice in the *b* direction. The distance between neighboring boron atoms is 8.862(17) Å. The molecular organization defines infinite channels parallel to the *a* direction which accommodate disordered solvent molecules. Unlike fluoro-SubPcs,[13] the molecular shape of compounds **2** and **4** (inverted umbrella) prevents columnar stacking of the molecules.

The absorption spectra of all compounds show a strong Soret band near 300 nm ($\varepsilon \approx 30\,000\,\mathrm{M^{-1}\,cm^{-1}}$) and an intense Q band around 565 nm ($\varepsilon \approx 50\,000$–$89\,000\,\mathrm{M^{-1}\,cm^{-1}}$), as for simple SubPcs bearing axial chlorido ligands.[14] The axial substituents have only a very small effect on the position of the Q band ($\lambda_{\mathrm{abs}} = 567$ nm for **1**–**3** and $\lambda_{\mathrm{abs}} = 573$ nm for the Cl-SubPc precursor). The electronic absorption spectra of **3** and **6** reflect the presence of the electronically independent SubPc and ethynylgallate (λ_{max} at 271 and 304 nm) or ethynylpyrene subunits (λ_{max} at 386 and 414 nm) without noticeable absorption shifts, which is consistent with the absence of orbital overlap between the SubPc organic core and the axially connected nuclei (Figure 3).

For all the new compounds, excitation in the low energy absorption band around 567 nm lead to a strong emission at

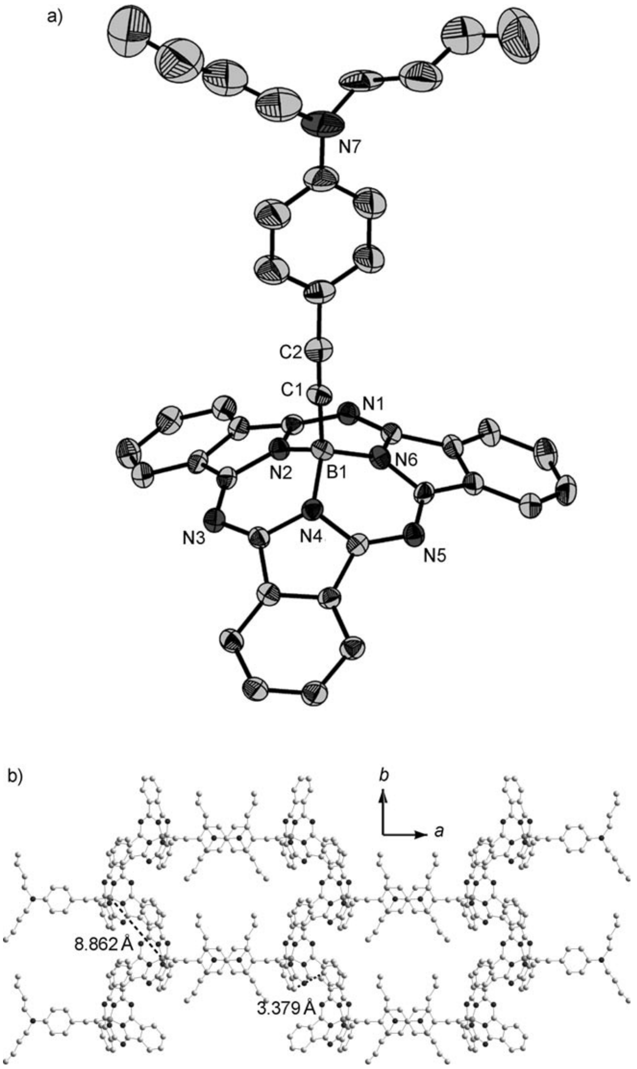


Figure 2. a) ORTEP view of compound **4** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected data: B1–N2 1.496(9), B1–N4 1.508(11), B1–N6 1.487(9), B1–C1 1.565(10) Å and N2-B1-N4 102.5(5), N4-B1-N6 102.1(5), N6-B1-N2 103.6(5), N2-B1-C1 114.6(5), N4-B1-C1 118.3(5), N6-B1-C1 113.9 (5)°. b) Views showing the crystal packing in the *ab* plane.

575 nm, with quantum yields in the range 12–23 % (Table 1) and Stokes shifts of 245 cm^{-1}, which are comparable with those of related SubPcs.[15] The fluorescence spectra show excellent mirror symmetry with the lowest energy absorption transition, which confirms that these transitions are weakly polarized and originate from the same state, as is typical of singlet emitters. Furthermore, the fluorescence decay profiles can be fitted to a single exponential decay, with fluorescence lifetimes of about 2 ns, which is also typical of a singlet excited state. For dyes **5** and **6**, excitation into the absorption band of the truxene and pyrene residues (at 340 and 414 nm respectively) leads principally to the characteristic emission of the SubPc fragment at 575 nm as well as a very weak emission signal from the polycyclic fragments ($\phi = 0.1\,\%$ residual fluorescence at 380 nm for compound **5** and $\phi = 2\,\%$ residual fluorescence at 477 nm for compound **6**; see Table 1 for the

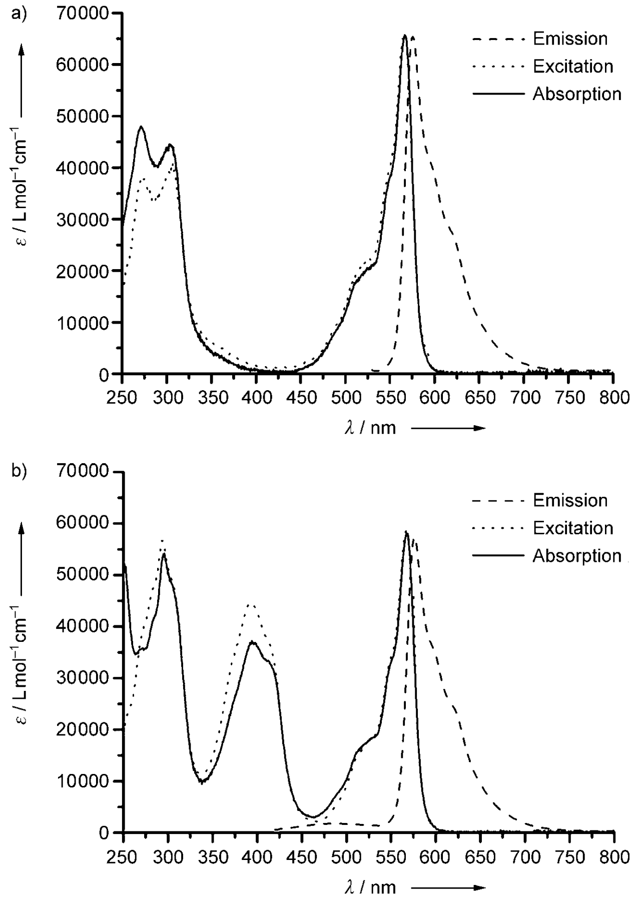


Figure 3. Absorption, emission and excitation spectra in dichloromethane of a) **3** and b) **6**.

Table 1: Spectroscopic data (298 K) for SubPc derivatives.[a]

Cmpd	λ_{abs} [nm]	ε [$M^{-1}\,cm^{-1}$]	λ_F [nm]	Φ_F[b] [%]	τ_F [ns]	k_r[c] [$10^7\,s^{-1}$]	k_{nr}[c] [$10^8\,s^{-1}$]	Stokes shift [cm^{-1}]
1	567	53300	575	15	2.8	5.36	3.03	245
2	567	88000	575	17	3.3	5.15	2.51	245
3	567	65600	575	12	2.9	4.13	2.24	245
4	566	76000	581	1	0.4	0.25	24.8	456
4+H^+	–	–	581	17	1.4	1.21	5.90	456
5	568	89400	575	16	2.6	6.15	3.23	214
	340	68500	575	13	–	5.00	3.35	12000
			380	0.1	n.d.	–	–	–
6	567	59000	575	23	3.0	6.00	2.73	245
	414	0.665	575	18	–	7.66	2.56	6760
			477	2	n.d.	–	–	–
A	324	21500	380	32	17.8	0.18	38.2	–
	308	41400						
B	410	36700	484	85	2.6	3.27	57.7	–
	387	37700						

[a] Determined in degassed dichloromethane solution. n.d. = not determined. [b] Determined using rhodamine 6G ($\phi_F = 0.86$ in methanol[20]) and cresyl violet ($\phi_F = 0.50$ in ethanol[20]) as reference. All ϕ_F values were corrected for changes in refractive index. [c] Calculated using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1-\Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency.

fluorescence of the reference compounds). The fluorescence excitation spectra perfectly match the absorption spectra, confirming a very efficient cascade energy transfer from the truxene or pyrene residues to the SubPc emitter (Figure 3). An energy transfer efficiency of > 96 % can be derived from the quantum yield measurements. For the pyrene derivative **6**, the more favorable spectral overlap is responsible for the almost quantitative energy transfer. The virtual Stokes shifts increase from 250 cm^{-1} in Cl-SubPc to 6800 cm^{-1} for **5** and 12000 cm^{-1} for **6**.[15]

When strongly electron-donating groups such as $n\mathrm{Bu_2N}$ are linked to the SubPc by an ethynylphenyl unit (compound **4**), marked quenching is observed (94 % of the initial fluorescence). The calculated driving force for photoinduced electron transfer from the $n\mathrm{Bu_2N}$ fragment to the SubPc* (excited state) is $\Delta G = -0.31$ eV, calculated by using the Rehm–Weller equation,[16] with the assumption that the electrostatic factor is negligible and that the emitting Q-band level lies at 2.22 eV. The redox potentials required for these calculations are given in Table 2. Addition of excess $HClO_4$ in CH_2Cl_2 restores the emission intensity, giving a quantum yield of 17 % and a corresponding increase of k_r from $0.25 \times 10^7\ s^{-1}$ to $1.2 \times 10^7\ s^{-1}$.

Stepwise addition of $HClO_4$ in dichloromethane progressively enhances the fluorescence intensity of **4** (Figure 4). The changes in the absorption spectra upon addition of the acid showed a well-defined isosbestic point that is indicative of a single equilibrium step. This was analyzed using SPECFIT[17] gave $\log \beta = (4.3 \pm 0.1)$, a value similar to analogous dialkylamino derivatives.[18] Protonation of the $n\mathrm{Bu_2N}$ fragment inhibits the photoinduced electron transfer (PET) process and the initial fluorescence is restored. Several protonation/deprotonation cycles were achieved, with no noticeable decomposition of compound **4**.

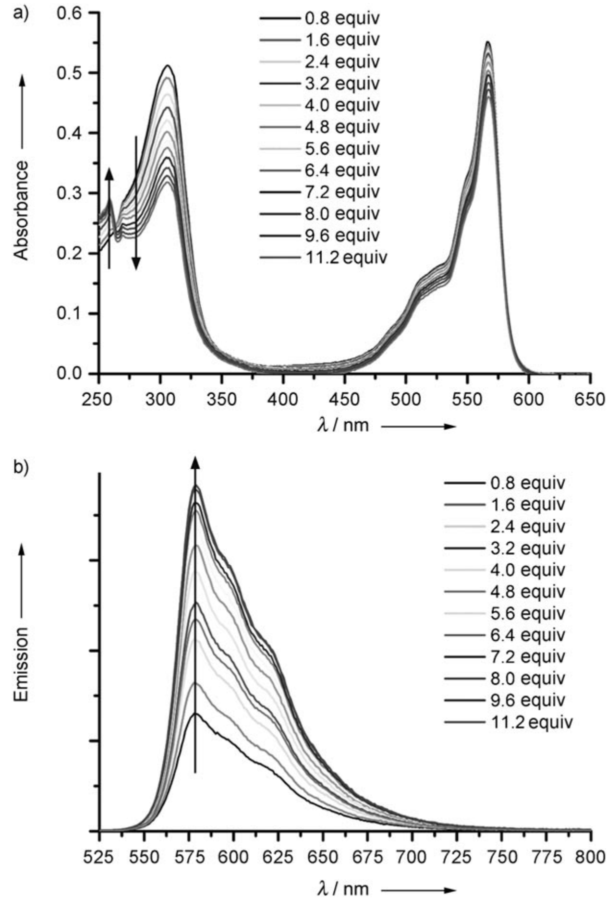


Figure 4. Titration of **4** with $HClO_4$ in CH_2Cl_2 in $n\mathrm{Bu_4NPF_6}$ (0.01 M) a) by absorption and b) by fluorescence $\lambda_{exc} = 500$ nm.

Table 2: Electrochemical data and optical HOMO–LUMO gaps.[a]

Cmpd	Redox potentials [V] versus SCE (ΔE_p [mV])		HOMO–LUMO gap [eV]	
	E_{ox}	E_{red}	CV	UV/Vis[b]
1	+0.91 (60)	−1.09 (70) −1.64 (80)	2.00	2.15
2	+0.91 (60)	−1.08 (70) −1.62 (ir.)	1.99	2.15
3	+0.94 (70)	−1.11 (70) −1.71 (ir.)	2.05	2.15
4	+0.99 (ir.) +0.77 (ir.)	−1.14 (70) −1.68 (80)	1.91	2.13
4+$\mathbf{H}^{+[c]}$	+0.99 (ir.)	–	–	2.13
5	+0.96 (ir) +1.45 (ir.)	−1.10 (60) −1.64 (ir.)	2.06	2.15
6	+0.96 (ir.) +1.20 (ir.)	−1.18 (60) −1.61 (60) −1.77 (ir.) −1.82 (ir.)	2.14	2.15
A	+1.35 (ir.)	−1.33 (80)	–	–
B	+1.16 (ir.)	−1.80 (ir.)	–	–

[a] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solution, containing $n\mathrm{Bu_4NPF_6}$ (0.1 M), at a solute concentration of ca. 1.5 mM and at 20 °C. Potentials were standardized versus ferrocene (Fc) as internal reference and converted to the saturated calomel electrode (SCE) scale assuming that $E_{1/2}$ (Fc/Fc^+) = +0.38 V ($\Delta Ep = 60$ mV) vs. SCE. Error in half-wave potentials is ±10 mV. Irreversible processes are indicated as ir. All reversible redox steps result from one-electron processes. [b] Calculated from the Q band transition. [c] In the presence of CF_3COOH vapor. The cathodic processes are masked by the reduction of the protons.

The axial grafting of aryl residues to the boron atom facilitates the oxidation of the SubPc to $\mathrm{SubPc}^{+\bullet}$ by 140 mV compared to the starting Cl-SubPc, whereas the reduction of the dye to the radical anion $\mathrm{SubPc}^{-\bullet}$ is cathodically shifted by 90 mV in most cases (Table 2).[19] Interestingly, the SubPc^{2-} dianion is also observed around −1.64 V but is not observed with the Cl-SubPc. The experimentally determined electrochemical HOMO–LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) gaps are consistent with the gaps determined by optical spectroscopy (Table 2). As would be expected by grafting pyrene and truxene fragments, additional redox processes are present, in particular the irreversible oxidations of pyrene at +1.20 V and truxene at +1.45 V. These results reflect trends found for related boron-substituted ethynyl derivatives, for which similar shifts of both redox processes have been observed.[12b]

In compound **4**, the $n\mathrm{Bu_2N}$ fragment is oxidized at +0.77 V. The addition of trace amounts of CF_3COOH during the cyclic voltammetry clearly resulted in the disappearance of the wave at +0.77 V (versus SCE), whereas the oxidation of the SubPc remains localized at the same potential (Table 2).

In summary, we have developed a general method for the engineering of axially modified 14-π-conjugated SubPcs. The use of alkynylaryl residues is an elegant means to simultaneously import solubility, polarizability, and strong electronic absorption. By grafting pyrene or truxene groups, efficient energy transfer to the SubPc occurs, which increases the virtual Stokes shifts to 6800 cm^{-1} for pyrene and to 12000 cm^{-1} for truxene substitution. Replacement of B−Cl by B−C≡CAr does not significantly perturb the HOMO–LUMO band gap (Eg ≈ 2.05 eV) but induces a translation to the anodic zone by approximately 100 mV. Grafting strong $n\mathrm{Bu_2N}$ electron-donating groups to the SubPc quenches its fluorescence by photoinduced electron transfer, however, stepwise protonation restores the fluorescence and this allows determination of the local pH. The chemistry at the boron atom of SubPc provides a methodology that is well suited to the construction of more complicated architectures bearing electron or hole transporting modules for application in light-emitting devices. The large Stokes shifts and the acid-triggered "switching on" of emission suggest that the new dyes might be useful as acid-sensing or acid-activated fluorophores.

Received: June 30, 2008

Keywords: alkynes · cross-coupling · energy conversion · luminescence · subphthalocyanines

---

[1] a) *Phthalocyanines Materials, Synthesis Structures and Function* (Ed.: N. B. McKeown), Cambridge University Press, Cambridge, **1998**; b) M. Hissler, A. Harriman, A. Khatyr, R. Ziessel, *Chem. Eur. J.* **1999**, *5*, 3366; c) *The Porphyrin Handbook*, *Vol. 13–16* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2002**; d) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2002**; e) *Fluorescence Spectroscopy in Biology: Advanced Methods and their Applications to Membranes, Proteins, DNA, and Cells* (Eds.: H. Martin, H. Rudolf, F. Vlastimil), Springer, Heidelberg, **2005**.

[2] a) G. Ulrich, C. Goze, M. Guardigli, A. Roda, R. Ziessel, *Angew. Chem.* **2005**, *117*, 3760; *Angew. Chem. Int. Ed.* **2005**, *44*, 3694; b) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891; c) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*, 1202; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184.

[3] M. Hanack, H. Heckmann, R. Polley, *Methoden Org. Chem. (Houben-Weyl)*, Vol. E9d, **1998**, p. 717.

[4] a) C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835; b) Y. Inokuma, A. Osuka, *Dalton Trans.* **2008**, 2517; c) Y. Inokuma, S. Easwaramorthi, S. Y. Jang, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 4918; *Angew. Chem. Int. Ed.* **2008**, *47*, 4840.

[5] S. H. Kang, Y.-S. Kang, W.-C. Zin, G. Olbrechts, K. Wostyn, K. Clays, A. Persoons, K. Kim, *Chem. Commun.* **1999**, 1661.

[6] M. V. Martinez-Diaz, B. del Rey, T. Torres, B. Agricole, C. Mingotaud, N. Cuvillier, G. Rojo, F. Agullo-Lopez, *J. Mater. Chem.* **1999**, *9*, 1521.

[7] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, T. Torres, *Synthesis* **1996**, 1139.

[8] B. del Rey, T. Torres, *Tetrahedron Lett.* **1997**, *38*, 5351.

[9] C. G. Claessens, D. González-Rodríguez, B. del Rey, T. Torres, G. Mark, H.-P. Schuchmann, C. von Sonntag, J. G. MacDonald, R. S. Nohr, *Eur. J. Org. Chem.* **2003**, 2547.

[10] a) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2000**, *122*, 6335; b) M. J. Bayer, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2002**, 2069; c) W.-L. Jia, D. Saong, S. Wang, *J. Org. Chem.* **2003**, *68*, 701; d) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi, K. Tamao, *Angew. Chem.* **2003**, *115*, 2082; *Angew. Chem. Int. Ed.* **2003**, *42*, 2036.

[11] a) B. Qian, S. W. Baek, M. R. Smith III, *Polyhedron* **1999**, *18*, 2405; b) L. Ding, K. Ma, G. Dürner, M. Bolte, F. Fabrizi de Biani, P. Zanello, M. Wagner, *J. Chem. Soc. Dalton Trans.* **2002**, 1566.

[12] a) G. Ulrich, C. Goze, M. Guardigli, A. Roda, R. Ziessel, *Angew. Chem.* **2005**, *117*, 3760; *Angew. Chem. Int. Ed.* **2005**, *44*, 3694; b) C. Goze, G. Ulrich, R. Ziessel, *J. Org. Chem.* **2007**, *72*, 313.

[13] M. S. Rodríguez-Morgade, C. G. Claessens, A. Medina, D. González-Rodríguez, E. Gutiérrez-Puebla, A. Monge, I. Alkorta, J. Elguero, T. Torres, *Chem. Eur. J.* **2008**, *14*, 1342.

[14] N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096.

[15] We define here a virtual Stokes Shift that correspond to the energy difference between the energy input and the energy output keeping in mind that by definition a real Stokes shift corresponds to the energy difference belonging to the same excited state.

[16] D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259.

[17] SPECFIT, G. A. Kriss in *Astronomical Data Analysis Software & Systems III*, *A. S. P. Conf. Series*, *Vol. 61* (Eds.: D. R. Crabtree, R. J. Hanisch, J. Barnes), Astronomical Society of the Pacific, San Francisco, **1994**, p. 437.

[18] M. Baruah, W. Qin, C. Flors, J. Hofkens, R. A. L. Vallée, D. Beljonne, W. M. Van de Auweraer, M. De Borggraeve, N. Boens, *J. Phys. Chem. A* **2006**, *110*, 5998.

[19] R. A. Kipp, J. A. Simon, M. Beggs, H. E. Ensley, R. H. Schmehl, *J. Phys. Chem. A* **1998**, *102*, 5659.

[20] J. Olmsted III, *J. Phys. Chem.* **1979**, *83*, 2581.