Synthesis and Nonlinear Optical, Photophysical, and Electrochemical Properties of Subphthalocyanines

B. del Rey,[†] U. Keller,[†] T. Torres,*[,†] G. Rojo,[‡] F. Agulló-López,*[,‡] S. Nonell,*[,§] C. Martí,[§] S. Brasselet,[⊥] I. Ledoux,[⊥] and J. Zyss*[,⊥]

Contribution from the Departments of Organic Chemistry C-I and Physics of Materials C-IV, Universidad Autónoma de Madrid (UAM), Cantoblanco, Madrid-28049, Spain, Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, 08017-Barcelona, Spain, and Department d'Electronique Quantique et Moléculaire, France Telecom, CNET Paris-B, 196, Avenue Henri Ravera, 92225 Bagneux, France

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Abstract: Novel boron(III) subphthalocyanines (SubPcs) soluble in organic solvents containing a variety of donor and acceptor substituent groups have been synthesized by boron trihalide-induced cyclotrimerization of adequately substituted derivatives of phthalonitrile in 1-chloronaphthalene. The choice of the substituents on the 1,2-dicyanobenzene derivatives has been made taking into account the high reactivity of the Lewis acid BCl_3 toward many functional groups. Considering this limitation, we set out to synthesize phthalodinitriles equipped with iodo, nitro, alkyl- or arylthio, alkyl- or arylsulfonyl groups that are sufficiently stable under the required reaction conditions and also provide an easily accessible set of acceptor/donor substituents. The quadratic and cubic hyperpolarizabilities of these compounds as well as their linear optical and electrochemical properties have been measured by several techniques, including EFISH (at two wavelengths), HRS, and THG, steady-state and time-resolved absorption and fluorescence, laser-induced optoacoustic calorimetry, time-resolved near-infrared emission spectroscopy, and cyclic voltammetry. β_{HRS} has been measured at 1.46 μm, where the contamination from the multiphoton-induced fluorescence can be ruled out. β_{HRS} reachs high values that markedly depend on substitution. It shows a clear enhancement with the acceptor character of the substituents, the highest values being obtained for the compounds bearing the strongest acceptor groups. They are comparable or even superior to many efficient second-order compounds. A main outcome of these results is that an adequate choice of the substituents offers a promising route for optimization of the quadratic response of the SubPcs. This kind of compounds is less prone to aggregation than their expanded analogues, the phthalocyanines, fluoresces with quantum yields ca. 0.25, lower than those typical for phthalocyanines, and has larger triplet quantum yields. The triplet-state lifetime is in the 100-μs time range, long enough for efficient oxygen quenching. Indeed, subphthalocyanines sensitize singlet molecular oxygen, $O_2(^1\Delta_g)$, with quantum yields ranging from 0.23 to 0.75. The ground-state oxidation potentials are similar to those of phthalocyanines, while the reduction potentials are clearly more negative; i.e., they are more difficult to reduce. In contrast, electronically excited subphthalocyanines are more easily oxidized than the corresponding phthalocyanines by ca. 500 mV which results in lower photostability, especially in polar solvents.

Organic materials are increasingly considered as a real alternative to inorganic compounds for nonlinear optical applications, such as parametric amplification and oscillation, and all optical modulation and switching. Their main advantages are high and ultrafast nonlinear optical (NLO) responses and low dielectric constants as well as the possibility of tailoring their physicochemical and NLO properties through molecular engineering. The first step in obtaining efficient organic materials is to design and synthesize molecules with high nonresonant molecular hyperpolarizabilities.[1] Whereas an electron-delocalized organic system is the single prerequisite for achieving a third-order nonlinear response, second-order nonlinear effects emanate only from noncentrosymmetric molecules, and their enhancement has mostly relied on push−pull systems.[2]

One particular promising route[3] for both second- and third-order NLO applications is provided by conjugated molecules related to phthalocyanines (Pcs). These are well-known planar compounds with excellent physicochemical properties, including high aromaticity, associated with their 18 π-conjugated electron system and very good thermal and chemical stability.[4] With regard to the third-order NLO response, high cubic hyperpolarizabilities γ have been recently measured, and good optical

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[†] Department of Organic Chemistry, UAM.

[‡] Department of Physics of Materials, UAM.

[§] IQS-Universitat Ramon Llull.

[⊥] CNET.

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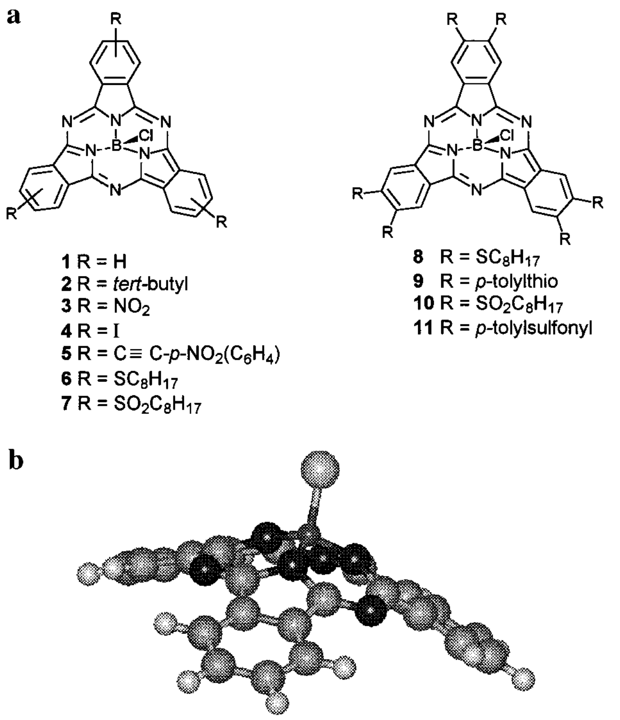

Figure 1. (a) Tri- and hexasubstituted subphthalocyanines **1**−**11**. (b) 3-D structure of **1** as determined from X-ray analysis.

limiting capabilities have been achieved.[3a] This makes them potentially useful for many third-order applications. On the other hand, metallophthalocyanines are not, generally, suitable for second-order applications because of their inversion symmetry. However, a few unsymmetric substituted Pcs have been prepared and their NLO properties studied, although very scarce information is still available on their second-harmonic generation (SHG) performance.[3,5,6]

Recently, a long-range research effort has been started on intrinsically noncentrosymmetric Pc derivatives called subphthalocyanines (SubPcs), whose chemical structure is illustrated in Figure 1a. Subphthalocyanines (SubPcs) are macrocycles formed by three coupled isoindole moieties having a delocalized 14 π-electron system, whose synthesis was first reported in 1972.[7] Unlike the related planar phthalocyanines, SubPcs have a cone-shaped structure (Figure 1b), as established by X-ray analysis,[8] which does not prevent them from having an aromatic nature.[9] Twenty years later, SubPcs are again receiving considerable attention as excellent building blocks for the synthesis of unsymmetric phthalocyanines[10,11] and as materials for nonlinear optics.[3b,12−14] Recently, their preparation and reactivity have been reviewed.[15] Interestingly, to the best of our knowledge, no report on their photophysical properties has ever been published, despite their intense pink color and obvious fluorescence. The ever-increasing use of Pcs as sensitizers in photooxidation and photoinduced electron-transfer processes suggests that SubPcs might be of interest for these applications.

In view of the nontrivial synthesis[15] of the Subpcs, it is not surprising that only very few examples of substituted derivatives have been reported so far and studies on their nonlinear optical properties are even more limited in number.[12−14] Large third-order susceptibilities, $\chi^{(3)}$, have been measured[12] on evaporated thin films of unsubstituted SubPc **1** by third-harmonic generation (THG). Moreover, high β_{HRS} values have been inferred for substituted compounds **2** and **3** from hyper-Rayleigh scattering (HRS) experiments.[13] On the other hand, the electric field-induced second-harmonic (EFISH) generation yield from the same substituted molecules was found to be very low and comparable to that for the unsubstituted molecule **1**. For this reason, the good HRS results were attributed to a dominant octupolar contribution[3b,16] arising from the cone-shaped trigonal geometry.[8] The highest value of β_{HRS} was measured for derivative **3** bearing electron-attracting groups ($-NO_2$), whereas smaller values were obtained for unsubstituted SubPc **1** and a derivative with electron-donating groups (*tert*-butyl), **2**. Evaporated and spin-coated films of **3** have been also studied by SHG.[14] This very promising behavior has prompted us to carry out a detailed and systematic study of the NLO response of SubPcs with special emphasis on elucidating the role of donor and acceptor substituents. In the present paper, we report on the synthesis of novel tri- and hexasubstituted Subpcs, the characterization of their photophysical, photosensitizing, and electrochemical properties, and a comparative study of the nonlinear optical behavior of several of these compounds (**3**−**11** in Figure 1a). EFISH (at two frequencies), THG, and HRS experiments have been performed in order to provide useful data on the second- and third-order NLO responses. In addition, we report that these SubPcs possess rich photophysical and electrochemical properties that, combined with the unusual cone-shaped geometry and the resulting lower tendency to aggregate, make them interesting photosensitizers.

Results and Discussion

Synthesis and Spectroscopic Characterization. Following a procedure initially reported by Meller and Ossko,[7] the synthesis of Subpcs is commonly carried out by boron trihalide-induced cyclotrimerization of adequately substituted derivatives of phthalonitrile in 1-chloronaphthalene. Accordingly, the choice of the substituents on the 1,2-dicyanobenzene derivatives to be

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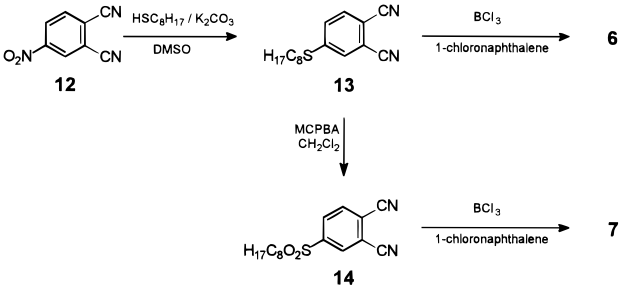
Scheme 1. Synthesis of the Trisubstituted Subphthalocyanines **6** and **7**



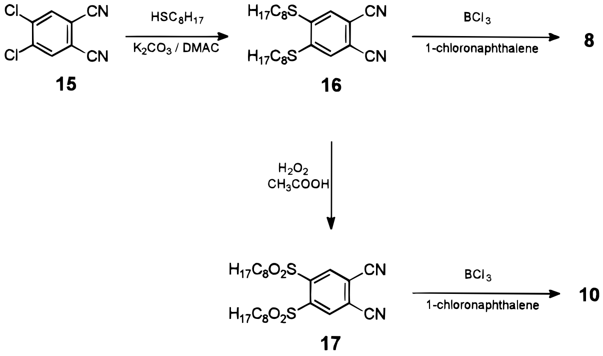
employed must take into account the high reactivity of the Lewis acid BCl_3 or BBr_3 toward functional groups such as ether, alkyl, etc. Considering this limitation, we set out to synthesize phthalodinitriles equipped with iodo, nitro, alkyl- or arylthio, alkyl- or arylsulfonyl groups that not only are expected to be sufficiently stable under the required reaction conditions but also provide an easily accessible set of acceptor/donor substituents.

Subphthalocyanines **1**−**4** have been previously described.[15] Compound **6** was prepared from 4-nitrophthalonitrile[17a] (**12**) in two steps (Scheme 1). Thus, treatment of **12** with octanethiol and potassium carbonate in dimethyl sulfoxide (DMSO) as solvent[17b−d] afforded the thioether **13**[17c,d] in high yield. Compound **13** was cyclotrimerized in the presence of boron trichloride (BCl_3) in 1-chloronaphthalene[15] under argon to afford **6** in 27% yield as a sticky residue after purification by column chromatography on alumina. On the other side, the preparation of **7** was carried out from **13** by oxidation with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane to give **14** in good yield, which was further reacted with BCl_3. Compound **7** was obtained in low yield (13%) after purification by solvent extraction.

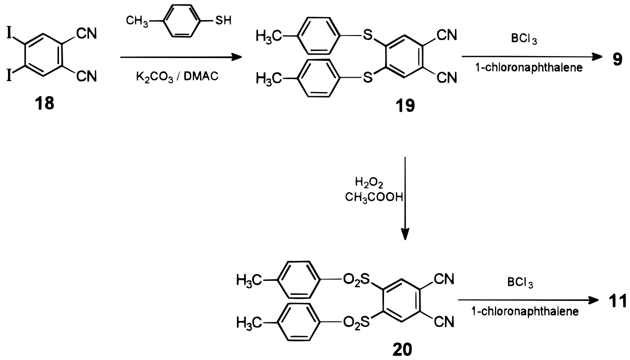
Compounds **6** and **7** are each mixtures of two constitutional isomers with symmetries C_1 and C_3. The regioisomers could not be separated by chromatography, but their presence was clearly observed by ^1H NMR. A 3:1 ratio of both isomers was estimated from their ^1H NMR spectra. This fact is in agreement with previous results obtained by us for related compounds,[11b] thus confirming that a nonregioselective statistical condensation of the phthalonitrile subunits has taken place in the formation of **6** and **7**.

Compound **8** (Scheme 2) was prepared from 4,5-dichlorophthalonitrile (**15**)[18] in two steps. Treatment of **15** with octanothiol and potassium carbonate using dimethylacetamide (DMAC) as solvent afforded dithioether **16** in high yield. The use of DMSO, usually employed in this kind of substitution reaction,[17b,18] is discouraged in this particular case since it is known to effect readily the oxidative dimerization of thiols.[19] Compound **16** was cyclotrimerized in the presence of boron trichloride in the usual way.[15] On the other hand, the preparation of **10** (Scheme 2) was achieved from **16** by oxidation with hydrogen peroxide in acetic acid to give **17**, which was further reacted with boron trichloride.

Scheme 2. Synthesis of Hexasubstituted Subphthalocyanines **8** and **10**



Scheme 3. Synthesis of Hexasubstituted Subphthalocyanines **9** and **11**



Subphthalocyanine **9** (Scheme 3) was prepared from diiodophthalonitrile (**18**)[20] also in a two-step sequence. Compound **18** was treated with 4-methylthiophenol and potassium carbonate in DMSO as solvent by modification of a known procedure[18] to afford the thioether **19** in good yield. Compound **19** was then reacted with BCl_3 in the usual way[15] to give **9.** On the other hand, the preparation of **11** was readily achieved from **19** by oxidation with MCPBA to give **20**, followed by cyclotrimerization reaction of this in the presence of BCl_3. Compounds **9** and **11** were obtained in 28 and 25% yield, respectively, the first as a sticky residue. Moderate to low yields are typical in the preparation of subphthalocyanines.[15]

Highly conjugated subphthalocyanine **5**[21a] was obtained by a metal-mediated cross-coupling methodology.[21b] Thus, *p*-nitroethynylbenzene[21c] (**21**) was reacted with triiodosubphthalocyanine **4** in the presence of bis[triphenylphosphine]palladium(II) dichloride and copper(I) iodide in oxygen-free triethylamine at room temperature, affording **5** in moderate yield (Scheme 4).

The overall shape of the UV−visible spectra of subphthalocyanines is similar to that of the metallophthalocyanines, and so dominated by two intense bands: the Q-band around 560 nm (in the unsubstituted compound **1**) and the Soret (B) transition in the UV region of the spectrum around 300 nm. (Figure 2). The bands are blue-shifted compared to those of metallophthalocyanines owing to the smaller conjugated system (14 vs 18 π electrons) and have lower absorption coefficients.

The position of the Q-band in SubPcs can be clearly red-shifted (bathochromic shift) with regard to the unsubstituted derivative by introducing electron-donor substituents (**2**, **6**, **8**,

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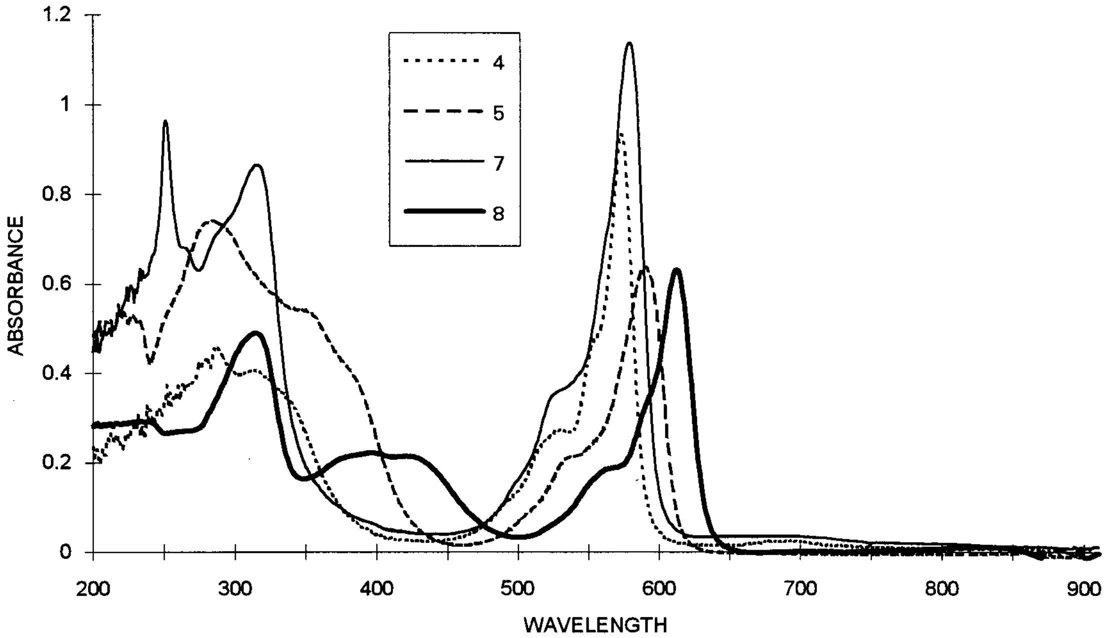

Figure 2. UV−vis absorption spectrum of subphthalocyanines **4**, **5**, **7**, and **8** in chloroform solution (2.5 × 10^{-5}, 1.7 × 10^{-5}, 7.4 × 10^{-6}, and 2 × 10^{-5} M, respectively).

Scheme 4. Synthesis of Trisubstituted Subphthalocyanine **5**

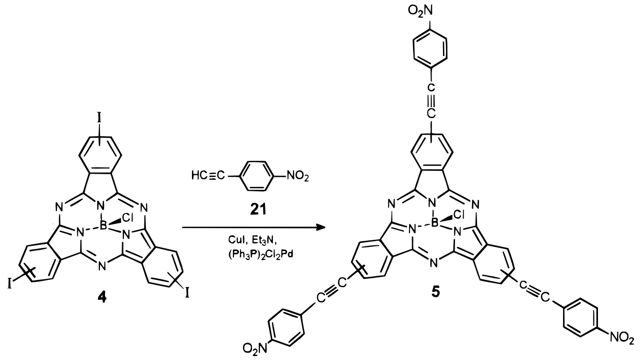

Table 1. Experimental Data Obtained from EFISH, THG, and HRS Experiments for Compounds **4**−**11**[a]

compd	λ_{max} (nm)	μ_0 (D)	γ_{EFISH} (10^{-34} esu) 1.9 μm	γ_{EFISH} (10^{-34} esu) 1.34 μm	γ_{THG} (10^{-34} esu), 1.34 μm	β_{HRS} (10^{-30} esu), 1.46 μm
3	586	5.5	−8.5	16	−13	144.3
4	573	5.3	−7.3	4.3	−5.8	164.5
5	590	10.1	−6	7	−14	38
6	584	6.7	−3.7	9.7	−23.4	76.5
7	570	7.6	−6.6	22.3	−18	168.5
8	603	15	−3	13	−106	40
9	607	4.8	−8	13.6	−70	64.3
10	579	14.8	−15	80	−27	260
11	587	8.6	−13.4	130	−1.6	211.5

[a] The λ_{max} corresponding to the Q-band transition and the measured ground-state dipole moment are also included.

and **9**). The same effect, but less important, takes place by introduction of electron-acceptor substituents in the SubPc (**3**, **4, 5, 7**, **10**, and **11**). The hexasubstituted SubPcs show larger red shifts (up to 40 nm for **9**) than the trisubstituted ones, probably reflecting a geometrical distortion of the outer benzo rings. Figure 2 shows the UV−visible absorption spectra in chloroform solution of SubPcs **4**, **5**, **7**, and **8** as representative examples of the compounds studied in this paper. The curious observation that bathochromic shifts of the Q-band are found for both donor and acceptor substituents may indicate a distortion of the SubPc geometry. This behavior is well documented for related porphyrins and phthalocyanines.[4,22] A new transition between the Soret and the Q-bands appears in the UV−visible spectrum of compounds bearing thioether groups. This band appears at 413 nm for **8**. Similar absorptions are also observed for **6** and **9** (not represented in Figure 2).

Unlike phthalocyanines, SubPcs remain monomeric in $CHCl_3$ solutions, even at concentrations of 1 mM; i.e., they have a remarkably lower tendency toward aggregation. This is a consequence of the nonplanar geometry and is of great advantage for applications as photosenzitizers, as aggregation invariably results in the deterioration of the photophysical properties.

All the compounds were characterized by NMR, IR, MS-FAB or MS-EI, UV−visible, and elemental analysis (see Experimental Section).

Nonlinear Optical Properties. The data for all investigated molecules obtained by the various NLO techniques are summarized in Table 1, together with the values for the permanent dipole moments (μ_0). It appears that most molecules are moderately polar, whereas **5**, **8**, and **10** are more strongly polar ($\mu_0 \geq 10$ D).

Let us first discuss the EFISH data taken at two fundamental wavelengths: 1.9 and 1.34 μm. γ_{EFISH} values at 1.9 μm are negative and do not show large differences among the various molecules. On the other hand, for 1.34 μm, the EFISH hyperpolarizability becomes positive, and measured values become strongly dependent on the particular compound. They are quite high for the molecules having acceptor substituents and reach a very remarkable value for **10** and particularly for SubPc **11**. On the other hand, molecules having donor substituents (**6**, **8**, and **9**) show rather small γ_{EFISH} values. These are in the same range as those reported for some unsymmetrically substituted Pcs.[6]

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All the above γ_{EFISH} data include an electronic γ_e (-2ω: 0, ω, ω) contribution, together with an orientational term proportional to $\mu\bullet\beta = \mu_0\beta_z$, where β is the vector part of the β_{ij} tensor and β_z its projection on μ. To separate this orientational contribution and calculate β_z, the electronic component γ_e should be known or considered negligible. This last possibility does not appear reasonable in view of the comparable values obtained for γ_{EFISH} and γ_{THG} (see Table 1), to be discussed below.

Let us now comment on the HRS results obtained at $\lambda = 1.46$ μm, where the possible spurious multiphoton-induced luminescence can be ruled out. The β_{HRS} values are also strongly dependent on the donor/acceptor character of the substituents and show the same trend as that previously described for γ_{EFISH} at $\lambda = 1.34$ nm. The highest values ($\sim 2 \times 10^{-28}$ esu) are reached for the molecules containing the electron acceptor groups (**3**, **4**, **7**, **10**, and **11**), whereas much lower values are measured for the case of electron-donor groups (**6**, **8**, and **9**). It is even remarkable that these lower values correspond to more resonant conditions than those for acceptor groups, due to the clear red shift of the Q-band associated with the donor groups. Note that the value, now measured at 1.46 μm, for **3** is remarkably lower than that previously reported at 1.34 μm.[13] This is possibly due to residual fluorescence contamination at the latter wavelength that could not be avoided in our previous setup.

As a summary, one can state that the β values measured for SubPcs are reasonally high in comparison to those reported for most organic compounds[23] and clearly superior to those available for related unsymmetrically substituted porphyrins.[24b] However, we should mention that very high HRS values have been obtained recently for some push−pull arylethynyl porphyrins,[24c] suggesting further optimization possibilities for SubPcs.

With regard to the cubic hyperpolarizability data, γ_{THG}, the values obtained are negative and markedly lower than those reported for symmetric phthalocyanines[25] but quite comparable to those for some unsymmetric Pcs.[6] This could indicate a decrease in the π-conjugation related to the smaller aromaticity of SubPcs in comparison to Pcs. On the other hand, they show a rather opposite trend with the substituents from that found for the quadratic polarizability β. In fact, the highest γ_{THG} values are obtained for those compounds, **6**, **8**, and **9**, containing donor substituent groups. This behavior may be due to the large red shift of the Q optical absorption band that should increase the resonant behavior at 2ω. Moreover, these compounds show an additional band at ca. 400 nm that is strongly resonant at the third-harmonic frecuency and so should also contribute to the enhancement.

Photophysical and Electrochemical Properties. Figure 3 shows the normalized absorption and fluorescence spectra of **1** in benzene. The intersection of both curves was taken as the energy contents of the first excited singlet state, E_S. The small Stokes shift suggests minor geometry differences between the ground and excited states.

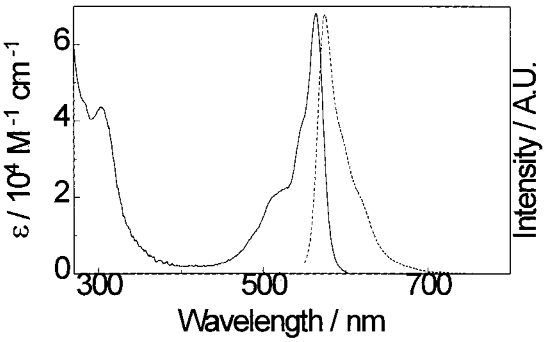

Figure 3. Absorption and fluorescence spectrum of SubPc **1** in benzene.

Subphthalocyanines are fluorescent, with quantum yields, Φ_F, ca. 0.25, about half the value observed for related phthalocyanines, e.g., $\Phi_F = 0.58$ for AlPcCl.[26] Clearly, nonradiative deactivation channels, i.e., internal conversion and intersystem crossing, are more efficient for SubPcs. The 10-fold decrease for SubPc **4** is readily explained on the basis of the highly efficient intersystem crossing characteristic of heavy-atom-substituted aromatic compounds.[27] The lifetimes of the excited singlet states, τ_S, measured by the single-photon-counting technique, are ca. 3 ns for all compounds but **4**, again about half the value for phthalocyanines (see Table 2).

Intersystem crossing to the triplet state occurs in high yield, as demonstrated by transient absorption experiments. Thus, transients are observed throughout the visible spectrum that are identified as triplet states owing to their lifetime sensitivity to oxygen and the concomitant production of singlet oxygen, $O_2(^1\Delta_g)$ (see below). Figure 4 shows the triplet-minus-singlet absorption spectrum of **2** with a maximum at 460 nm and a minimum at 560 nm, corresponding to the S_0-to-S_1 absorption maximum. The transients decay following first-order kinetics, with lifetimes, τ_T, ranging from 82 μs for **1** to 157 μs for **9** in argon-saturated solutions. Compound **4** shows a shorter lifetime, which can be rationalized again in terms of heavy-atom induced intersystem crossing T_1-S_0. For all compounds, the decay rate constants increase linearly with oxygen concentration, which allows the derivation of the bimolecular quenching rate constants, $k_q^{O_2}$, through the Stern−Volmer treatment. The values observed are typical for aromatic hydrocarbons.[28]

Failing to observe any phosphorescence even in 1-iodopropane at 77 K, the energy level of the triplet state, E_T, was estimated using the correlation described by Dreeskamp *et al.*[29] between the rate constant of fluorescence quenching by 1-iodopropane, k_q^{Ipr}, and the energy gap between the first excited singlet state and the nearest lower triplet state (Figure 5). This correlation was originally used for aromatic hydrocarbons but has been recently used for tetrapyrrolic compounds as well.[30] While the values obtained are, in principle, upper limits for E_T, the triplet quantum yield values, Φ_T, calculated from the product $\Phi_T E_T$ by LIOAC, are consistent with the singlet oxygen quantum yield data (see below and Table 2). The singlet-to-triplet energy gap (30−40 kJ mol^{-1}) is significantly smaller than

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Table 2. Summary of Photophysical (in Benzene) and Electrochemical (in CH_2Cl_2) Properties of the SubPcs Studied[a]

	1	2	3	4	6	7	9	11	AlPcCl
λ_{max}/nm	564	570	586	572	586	573	606	591	680^b
log(ϵ_S/M^{-1} cm^{-1})	4.8	4.7	4.5	4.7	4.7	4.5	4.9	4.6	5.1^b
E_S/kJ·mol^{-1}	209	209	203	208	202	207	195	200	174^b
Φ_F	0.25	0.16	0.20	0.013	0.25	0.18	0.24	0.23	0.58^b
τ_s (Ar)/ns	3.3	2.8	3.2	<0.5	2.8	3.1	2.9	2.9	6.8^b
k_qIPr/10^7 M^{-1} s^{-1}	30	13	8.0	20	49	11	40	8.9	
E_T/kJ·mol^{-1}	175	166	154	169	173	162	164	152	116^b
Φ_T	0.62	0.55	0.49	0.77	0.62	0.25	0.69	0.42	0.4^b
τ_T (Ar)/μs	82	127	109	56	130	144	157	132	500^b
λ_{max}(T−S)/nm	450	460	470	440	460	460	480	480	490^c
$\Delta\epsilon_{T-S}$/10^4 M^{-1} cm^{-1}	1.32	1.19	1.38	1.13	1.35	1.21	1.10	1.43	2.66^c
$k_q^{O_2}$/10^9 M^{-1} s^{-1}	1.79	0.88	1.33	1.15	1.46	0.95	1.18	1.17	
F_D	0.61	0.47	0.46	0.74	0.61	0.23	0.64	0.30	0.36^d
k_qS/10^7 M^{-1} s^{-1}	3.3	15	36	20	4	9.5	3.3	41	
$E_{1/2}(S^+/S)/V^e$	1.04	0.98	1.34	1.13	0.95	1.27	1.02	1.29	0.96^b
$E_{1/2}(S/S^-)/V^e$	−1.05	−1.11	−0.57	−0.92	−1.09	−0.70	−0.97	−0.78	-0.66^b
$E_{1/2}(S^+/{}^3S^*)/V^{e,f}$	−0.77	−0.74	−0.26	−0.62	−0.84	−0.41	−0.68	−0.28	-0.24^b
$E_{1/2}({}^3S^*/S^-)/V^{e,g}$	0.76	0.61	1.03	0.83	0.70	0.98	0.73	0.79	0.56^b

[a] Data for AlPcCl are given for comparison. See text for the use of abbreviations. [b] Reference 26. [c] Reference 44. [d] For several sulfonic acid derivatives, ref 35. [e] Versus the AgCl/Ag electrode. [f] Calculated as $E_{1/2}(S^+/S) - E_T/F$, where F is the Faraday constant. [g] Calculated as $E_{1/2}(S/S^-) + E_T/F$.

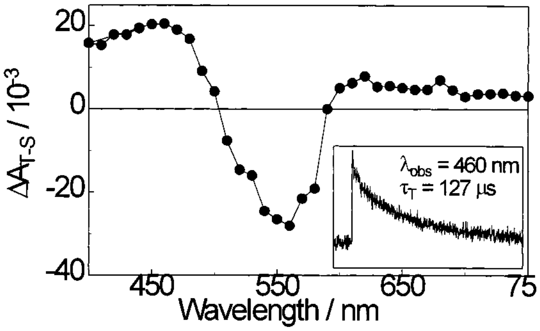

Figure 4. Triplet-minus-singlet absorption spectrum of **2** in argon-saturated benzene. Inset: Transient absorption at 460 nm. λ_{exc} = 337 nm.

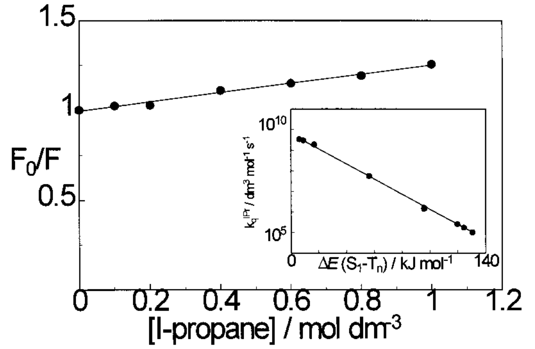

Figure 5. Stern−Volmer plot for **2** fluorescence quenching by 1-iodopropane in benzene. Inset: Dreeskamp plot of the quenching rate constant vs the singlet−triplet energy gap. Data from ref 29.

that of the phthalocyanines (50−70 kJ mol^{-1}).[26] Consistent with this, the intersystem crossing rate constants and quantum yields are larger.[31]

The quantum yield from triplet production, Φ_T, was determined by laser-induced optoacoustic calorimetry (LIOAC).[32,33] The difference between the pulsed-laser energy absorbed and the heat released within the first microsecond was ascribed to the energy stored in the long-lived triplet state, $\Phi_T E_T$, plus the energy lost by fluorescence, $\Phi_F E_F$, where E_F is the average fluorescence energy calculated over the entire emission spectrum. Using the above-determined values for E_T, Φ_F, and E_F, values for Φ_T (lower limit) could be readily calculated (see Table 2). The rate constants for intersystem crossing, calculated as $k_{isc} = \Phi_T/\tau_s$, decrease smoothly as the singlet-to-triplet energy gap increases and are more than 3-fold larger than that for chloroaluminumphthalocyanine, as anticipated. Internal conversion is also more effective than that for phthalocyanines, probably reflecting a lower degree of rigidity of the SubPcs.

The SubPcs are excellent photosensitizers and produce singlet oxygen, $O_2(^1\Delta_g)$, in large quantities, as measured by the $O_2(^1\Delta_g)$ phosphorescence at 1270 nm.[34] Singlet oxygen production occurs by exothermic energy transfer from the highly populated, long-lived triplet state, as shown by the triplet quenching experiments above. The quantum yields, Φ_Δ, agree with the Φ_T values derived from LIOAC, thus supporting the E_T values determined by the fluorescence method of Dreeskamp *et al.* SubPcs show slightly larger Φ_Δ values than the related phthalocyanines,[35] which make them interesting candidates for use in photosensitization processes, especially in situations where absorption in the red part of the spectrum is not required. SubPcs quench singlet oxygen with rate constants k_q^S ranging from 3.3 × 10^7 M^{-1} s^{-1} for **1** to 4.1 × 10^8 M^{-1} s^{-1} for **11** in benzene. The rate constants are, in general, higher than those observed for related macrocycles and increase with the ring oxidation potential, in contrast with the trend observed for related compounds.[36] This probably reflects specific substituent contributions that may offset the charge-transfer-mediated ring contribution to the quenching.

There is a report in the literature discussing photostability of SubPcs in solution.[8c] While SubPcs are, in general, less stable than the parent Pcs, decomposition is important only in polar solvents, stability being much more pronounced in apolar solvents. Indeed, we could not notice any decomposition along our photochemistry experiments in benzene.

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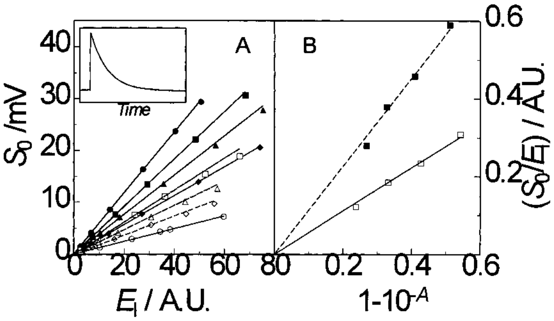

Figure 6. (A) Laser-energy dependence of the zero-time $O_2(^1\Delta_g)$ 1270-nm phosphorescence intensity in air-saturated benzene sensitized by **2** (open symbols) and PN (closed symbols) as a function of the solution absorbance. Inset: Typical transient luminescence signal for **2**. (B) Slopes of the energy plots as a function of the sample absorption. The ratio of slopes yields the ratio of Φ_Δs for sample and reference.

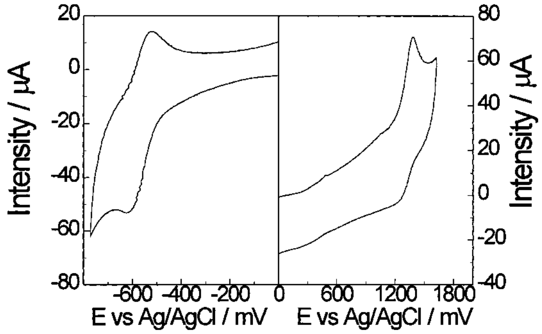

Figure 7. Cyclic voltammogram of **3** (50 mM) in N_2-saturated 0.1 M TBAP CH_2Cl_2. Scan rate: 100 mV s^{-1}.

The first oxidative and reductive half-wave potential of the SubPcs, $E_{1/2}(S^+/S)$ and $E_{1/2}(S/S^-)$, have been measured by cyclic voltammetry in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol·dm^{-3}). A voltammogram for **3** is shown in Figure 7. The oxidation and reduction potentials follow the trend one would anticipate from the substitution pattern, the nitro derivative **3** being the easiest to reduce by ca. 500 mV relative to **1**, followed by the sulfonyl derivatives **11** and **7** (by 350 and 270 mV, respectively). The oxidation potentials follow the same trend (see Table 2). While some degree of irreversibility is apparent in the voltammograms, our results for **1** (1.04 and −1.05 V vs AgCl/Ag, respectively) are in excellent agreement with those reported for a **1** analogue having a bromine atom in the axial position instead of chlorine (1.03 and −1.06 V, respectively).[8c] The oxidation potential is close to that of AlPcCl (0.96 V), while the reduction one is clearly more negative (−1.05 for SubPc **1** vs −0.66 V for AlPcCl);[26] i.e., SubPcs are, in general, more difficult to reduce. There are no data available for analogues to SubPcs **2**−**11**. For photoinduced electron-transfer processes, the relevant potentials are those of the excited states. Table 2 lists the oxidation and reduction potentials for the longer-lived triplet state, calculated adding (for reduction) or subtracting (for oxidation) the triplet energy contents E_T to the ground-state potentials.[26] The electronically excited subphthalocyanines are more easily oxidized than the phthalocyanines (by ca. 500 mV). This is consistent with the observation that SubPcs decompose under light in polar solvents,[8c] while Pcs are notorious for their stability.

Experimental Section

The UV−visible and infrared measurements were carried out respectively on Perkin-Elmer model Lambda 6 and Bruker IFS66V instruments. MS spectra were determined on a VG AutoSpec instrument. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer (200 and 50 MHz, respectively).

1,2-Dicyano-4-octylthiobenzene (13).[17c,d] A mixture of 4-nitrophthalonitrile (**12**)[17a] (10 g, 57.8 mmol) and octanethiol (8.4 g, 57.8 mmol) in DMSO (39 mL) was stirred at room temperature for 10 min. Then, dry potassium carbonate (8 g, 58 mmol) was added in small portions during 2 h. The mixture was vigorously stirred under argon atmosphere for 16 h. Water (50 mL) was added, and the product was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was washed with water (3 × 50 mL) and with a 5% solution of sodium carbonate (1 × 50 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed (SiO_2, CH_2Cl_2/hexane 4:1) to afford 13 g (83%) of **13**.

Mp: 32−35 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.88 (t, 3H), 1.7−1.2 (m, 12H), 3.0 (t, 2H), 7.4 (d, 1H), 7.5 (dd, 1H), 7.6 (d, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.5, 132.8, 129.9, 129.7, 116.1, 115.5, 115.1, 110.5, 31.8, 31.7, 29.0, 28.9, 28.7, 28.1, 22.5, 14.0 ppm. EI-MS: *m/z* 272 [M^+, 100]. IR (KBr): ν 721, 2228 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2S$: C, 70.54; H, 7.40; N, 10.28; S, 11.77. Found: C, 70.21; H, 7.35; N, 10.0: S, 11.97.

1,2-Dicyano-4-octylsulfonylbenzene (14). To a solution of 1,2-dicyano-4-octylthiobenzene (**13**) (4 g, 14.7 mmol) in dry CH_2Cl_2 (17 mL) cooled at 0 °C was slowly added *m*-chloroperbenzoic acid (12.7 g, 73.5 mmol) in CH_2Cl_2 (300 mL). The mixture was warmed to room temperature and vigorously stirred at this temperature overnight (12 h). A saturated sodium sulfite solution was then added, and the organic phase was extracted with CH_2Cl_2 (3 × 50 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure, and the solid was recrystallized from toluene/heptane (1:3) to give 3.3 g (74%) of **14** as a white solid.

Mp: 70−72 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.9 (m, 3H), 1.1−1.9 (m, 12H), 3.1 (m, 2H), 8.10 (d, 1H), 8.30 (d, 1H), 8.35 (dd, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.3, 134.6, 133.0, 132.5, 120.3, 117.3, 114.1, 114.0, 56.0, 31.6, 28.9, 28.2, 22.5, 22.4, 13.9 ppm. EI-MS: *m/z* 304 [M^+]. IR (KBr): ν 1113, 1137, 2239 cm^{-1}. Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20; S, 10.53. Found: C, 63.16; H, 6.49; N, 9.29; S, 10.78.

1,2-Dicyano-4,5-bis(octylthio)benzene (16). 4,5-Dichloro-1,2-dicyanobenzene[18] (**15**) (2.4 g, 12.2 mmol), dry K_2CO_3 (5.0 g, 36.2 mmol), and 30 mL of dimethylacetamide (DMAC) were placed in a 100-mL round-bottom flask, equipped with a magnetic stirrer, rubber seal, and globe. After a stream of argon had been passed through the slurry in order to remove oxygen, 4.7 mL of 1-octanethiol (3.9 g, 26.8 mmol) was added through a syringe, and the resulting mixture was stirred at 90 °C during 6 h. The reaction was poured into 100 mL of cold water, and the separated precipitate was collected and crystallized from cold ethanol (150 mL) to yield 4.0 g (79%) of 1,2-dicyano-4,5-bis(octylthio)-benzene (**16**) as white needles.

Mp: 62 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.89 (t, 6H), 1.1−1.6 (bm, 20H), 1.6−1.8 (m, 4H), 3.0 (m, 4H), 7.40 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0, 22.5, 28.0, 28.8, 29.0, 31.7, 32.7, 111.0, 115.6, 128.1, 144.2 ppm. MS (EI): *m/z* 416 [M^+, 100]. IR (KBr): ν 1114, 1226, 1348, 1460, 1562, 2229, 2852, 2923, 2957, 3077 cm^{-1}. Anal. Calcd for $C_{24}H_{36}N_2S_2$: C, 69.18; H, 8.71; N, 6.72; S, 13.39. Found: C, 69.12; H, 8.41; N, 6.53; S, 13.76.

1,2-Dicyano-4,5-bis(octylsulfonyl)benzene (17). 1,2-Dicyano-4,5-bis(octylthio) benzene (**16**) (1.2 g, 2.91 mmol) was dissolved in 35 mL of acetic acid at 90 °C. To the stirred solution was added a total of 15 mL of 33% H_2O_2 in 1-mL portions in the course of 4 h. The resulting turbid mixture was allowed to cool to room temperature and stirred overnight, and the white precipitate was collected by filtration, subsequently washed several times with water, and crystallized from ethanol (50 mL) to give 1.17 g (84%) of pure 1,2-dicyano-4,5-bis-(octylsulfonyl)benzene (**17**) as a white powder.

Mp: 75 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 0.89 (t, 6H), 1.1−1.5 (bs, 20H), 1.6−1.9 (m, 4H), 3.7 (m, 4H), 8.69 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0, 22.3, 22.5, 28.1, 31.6, 57.1, 113.1, 121.1, 137.4, 144.4 ppm. MS (EI): *m/z* 480 [M^+, 100]. IR (KBr): ν 1123, 1155, 1315, 1343, 1470, 2238, 2854, 2920, 2949, 3105 cm^{-1}. Anal. Calcd for $C_{24}H_{36}N_2O_4S_2$: C, 59.97; H, 7.55; N, 5.83; S, 13.34. Found: C, 59.98; H, 7.23; N, 5.63; S, 13.75.

1,2-Dicyano-4,5-*p*-tolylthiobenzene (19). A mixture of 4,5-diiodophthalonitrile (**18**)[20] (195 mg, 1 mmol), *p*-thiocresol (744 mg, 6 mmol), and (2.36 g, 32 mmol) of potassium carbonate in dry DMSO (2 mL) was heated at 90 °C for 30 min. The mixture was then cooled, ice was added carefully, and a yellow solid precipitated out. It was filtered, dried, and then purified by column chromatography (SiO_2, hexane/CH_2Cl_2, 3:10) to give 301 mg (81%) of **19**.

Mp: 195−197 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 2.4 (s, 3H), 6.9 (s, 1H), 7.3 and 7.4 (AA′BB′ system, 4H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.3, 111.1, 115.4, 124.5, 129.2, 131.3, 135.3, 141.2, 144.3 ppm. EI-MS: *m/z* 372 [M^+, 100]. IR (KBr): ν 760, 2226, 2919 cm^{-1}. Anal. Calcd for $C_{22}H_{16}N_2S_2$: C, 70.94; H, 4.33; N, 7.52; S, 17.21. Found: C, 71.01; H, 4.44; N, 7.49; S, 17.46.

1,2-Dicyano-4,5-*p*-tolylsulfonylbenzene (20). To a solution of 1,2-dicyano-4,5-*p*-tolylthiobenzene (**19**) (400 mg, 1.07 mmol) in dry CH_2Cl_2 (10 mL) cooled at 0 °C was slowly added *m*-chloroperbenzoic acid (1.84 g, 10.7 mmol) in dry CH_2Cl_2 (120 mL). The mixture was then warmed to room temperature and vigorously stirred for 2 days. Saturated sodium sulfite solution was then added, the product was extracted with CH_2Cl_2 (3 × 50 mL), and the organic phase was dried over sodium sulfate. The solvent was removed to yield 461 mg (99%) of **20** as a white solid.

Mp: 223−225 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.3 and 7.9 (AA′BB′ system, 4H), 8.78 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 113.2, 120.5, 129.0, 129.9, 136.2, 137.1, 145.9, 146.2 ppm. FAB-MS (3-NOBA): *m/z* 437 [M + H^+]. IR (KBr): ν 810, 921, 1082, 1159, 2250, 3090 cm^{-1}. Anal. Calcd for $C_{22}H_{16}N_2S_2O_4$: C, 60.54; H, 3.70; N, 6.42; S, 14.67. Found: C, 60.24; H, 3.74; N, 6.19; S, 14.26.

Chloro[2,9,16(2,9,17)-tri-*p*-nitrophenylethynylsubphthalocyaninato]boron(III) (Regioisomers Mixture) (5). A mixture of triiodosubphthalocyanine (**4**) (808 mg, 1 mmol), *p*-nitroethynylbenzene (**21**)[21c] (529 mg, 3.6 mmol), bis[triphenylphosphine]palladium(II) dichloride (21 mg, 0.03 mmol), and copper(I) iodide (3 mg, 0.015 mmol) in 10 mL of triethylamine was stirred for 1.5 h at room temperature under argon atmosphere. For working up, water was added, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the extracts were dried over Na_2SO_4. The solvent was removed, and the residue was purified by flash column chromatography (SiO_2) using CH_2Cl_2 as eluent, to yield 251 mg (29%) of tri-*p*-nitrophenylethynyl subphthalocyanine (**5**) (regioisomer mixture) as a violet powder.

Mp: >200 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 8.1 (m, 1H), 8.3 and 7.8 (AA′BB′ system, 4H), 8.9 (m, 1H), 9.1 ppm (m, 1H). FAB-MS (3-NOBA): *m/z* 865 $[M + H]^+$. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 590 (4.6), 540 (sh), 355 (4.5), 285 (4.6) nm. IR (KBr): ν 2210, 1592, 1331, 1185, 854 cm^{-1}. Anal. Calcd for $C_{48}H_{21}N_9O_6BCl$: C, 66.58; H, 2.45; N, 14.57. Found: C, 66.20; H, 2.64; N, 14.17.

Chloro[2,9,16(2,9,17)-trioctylthiosubphthalocyaninato]boron(III) (Regioisomers Mixture) (6). Dried 4-octylthiophthalonitrile (**13**) (460 mg, 1.79 mmol) was suspended in 1-chloronaphthalene (0.5 mL) under argon. Then BCl_3 (0.15 mL, 1.79 mmol, previously condensed at −78 °C) was added through a cannula with the help of a slightly positive argon pressure. The mixture was stirred for 10 min at room temperature and then heated at 80 °C for 15 min. After cooling, the black precipitate was washed with hexane; the solid was filtered and chromatographed (Al_2O_3, hexane/CH_2Cl_2, 1:1) to give 138 mg (27%) of **6** as a sticky violet compound.

^1H NMR (200 MHz, $CDCl_3$): δ 0.8 (m, 9H), 1.7−1.2 (m, 36H), 3.1 (m, 6H), 7.7 (d, 3H), 8.6 (m, 6H) ppm. FAB-MS (3-NOBA): *m/z* 862 [M^+], 863 [M + H^+]. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 584 (4.7), 540 (sh), 361 (4.2), 289 nm (4.6). IR (KBr): ν 968, 1730, 2952, 3853 cm^{-1}. Anal. Calcd for $C_{48}H_{60}N_6S_3BCl$: C, 66.76; H, 7.00; N, 9.73; S, 11.14. Found: C, 67.12; H, 7.40; N, 9.37; S, 10.69.

Chloro[2,9,16(2,9,17)-trioctylsufonylsubphthalocyaninato]boron(III) (Regioisomers Mixture) (7). BCl_3 (0.28 mL, 3.28 mmol), previously condensed at −78 °C, was added to a solution of 1,2-dicyano-4-octylsulfonylbenzene (**14**) (1 g, 3.28 mmol) in 1-chloronaphthalene (1 mL). The mixture was stirred at room temperature for 10 min and then was heated at 150 °C for 15 min. After cooling, the blue precipitate was washed with hexane and extracted with diethyl ether using a Soxhlet extractor for 2 h. The solvent was removed, and the solid was washed with cold methanol and filtered to yield 140 mg (13%) of **7** as a violet powder.

Mp: >250 °C. ^1H NMR (200 MHz, acetone-d_6): δ 0.8 (m, 9H), 1.0−2.5 (m, 36H), 3.5 (m 6H), 8.5 (m, 3H), 9.2 (m, 3H), 9.4 (m, 3H) ppm. FAB-MS (3-NOBA): *m/z* 958 [M^+], 959 [M + H^+]. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 570 (4.5), 523 (sh), 307 nm (4.6). IR (KBr): ν 970, 1140, 1302, 1734, 2855, 2925 cm^{-1}. Anal. Calcd for $C_{48}H_{60}N_6O_6S_3BCl$: C, 60.10; H, 6.30; N, 8.76; S, 10.01. Found: C, 60.34; H, 6.41; N, 9.01; S, 10.37.

Chloro[2,3,9,10,16,17-hexaoctylthiosubphthalocyaninato]boron(III) (8). Four milliliters of dry 1-chloronaphthalene was saturated at 0 °C with a slow stream of gaseous BCl_3. Three milliliters of this solution was rapidly transferred to a flask cooled in an ice bath and containing 1,2-dicyano-4,5-bis(octylthio)benzene (**16**) (450 mg, 1.08 mmol) under argon atmosphere. While stirring, the reaction mixture was allowed to warm to room temperature and subsequently kept at 60 °C for 40 min. For a nonaqueous work up, the reaction mixture was diluted with 30 mL of cold hexane and the black precipitate formed finely divided in the mixed solvents by sonication. The suspension obtained was freed from 1-chloronaphthalene by suction filtration through a layer of silica gel (5 cm) and repeated addition of hexane followed by elution of the subphthalocyanine with CH_2Cl_2. Removal of CH_2Cl_2 and of remaining traces of 1-chloronaphthalene was completed under high vacuum at 80 °C to give 120 mg (26%) of hexaoctylthiosubphthalocyanine (**8**) as a dark green sticky oil.

^1H NMR (200 MHz, $CDCl_3$): δ 0.86 (t, 18H), 1.4 (bm, 48H), 1.6 (m, 12H), 1.9 (m, 12H), 3.1 (m, 12H), 8.57 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 7.5, 23.1, 23.5, 28.7, 29.3, 32.4, 33.3, 33.7, 119.6, 128.3, 140.9, 149.1 ppm. FAB-MS (3-NOBA): *m/z* 1295 $[M + H]^+$. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 603 (4.9), 557 (4.4), 413 (4.5), 387 (4.5) 304 (4.8) nm. IR (KBr): ν 785, 978, 1081, 1419, 1435, 1461, 1596, 2852, 2924, 2954 cm^{-1}. Anal. Calcd for $C_{72}H_{108}N_6S_6BCl$: C, 66.71; H, 8.40; N, 6.48; S, 14.84. Found: C, 66.48; H, 8.08; N, 6.12; S, 14.80.

Chloro[2,3,9,10,16,17-hexa-*p*-tolylthiosubphthalocyaninato]boron(III) (9). Dried 1,2-dicyano-4,5-*p*-tolylthiobenzene (**19**, 400 mg, 1.07 mmol) was suspended in 1-chloronaphthalene (0.5 mL) under argon. Then BCl_3 (0.1 mL, 1.07 mmol, previously condensed at −78 °C) was added through a cannula with the help of a slightly positive argon pressure. The mixture was stirred for 10 min at room temperature and then was heated at 120 °C for 20 min. After cooling, the black precipitate was purified by column chromatography on Al_2O_3 in two steps (hexane, hexane/CH_2Cl_2, 1:1) to give 116 mg (28%) of **9** as a sticky violet compound.

^1H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 18H), 7.4 and 7.2 (AA′BB′ system, 12H), 8.37 (s, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.2, 122.9, 129.5, 130.7, 133.2, 139.3, 141.5, 149.1 ppm. FAB-MS (3-NOBA): *m/z* 1162 [M^+], 1163 [M + H^+]. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 607 (4.9), 550 (sh), 389 (4.3), 293 nm (4.6). IR (KBr): ν 975, 788, 809, 1413, 2850, 2918 cm^{-1}. Anal. Calcd for $C_{56}H_{48}N_6S_6BCl$: C, 64.45; H, 4.64; N, 8.05; S, 18.43. Found: C, 64.82; H, 4.81; N, 7.82; S, 17.92.

Chloro[2,3,9,10,16,17-hexaoctylsulfonylsubphthalocyaninato]boron(III) (10). Three milliliters of dry 1-chloronaphthalene was saturated at 0 °C with a slow stream of gaseous BCl_3. Three milliliters of this solution was rapidly transferred to the flask containing 1,2-dicyano-4,5-bis(octylsulfonyl)benzene (**17**) (203 mg, 0.42 mmol) under argon atmosphere at 0 °C. The stirred reaction mixture was allowed to warm to room temperature and subsequently kept at 70 °C for 2 h. For workup, the reaction mixture was diluted with 30 mL of cold hexane and the black precipitate formed finely divided in the mixed solvents by sonication. This suspension was freed from 1-chloronaphthalene by suction filtration through a layer of silica gel (5 cm) and repeated addition of hexane followed by elution of the subphthalocyanine with CH_2Cl_2. Removal of CH_2Cl_2 and of remaining traces of 1-chloronaphthalene was completed under high vacuum at 80 °C to give 23 mg (11%) of hexaoctylsulfonylsubphthalocyanine (**10**) as a violet solid.

^1H NMR (200 MHz, $CDCl_3$): δ 0.83 (t, 18H), 1.1−1.9 (bm, 72H), 3.8 (bm, 12H), 9.87 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0, 22.5, 22.6, 28.2, 28.9, 31.6, 57.2, 128.9, 132.6, 141.7, 150.5 ppm. FAB-MS (3-NOBA): *m/z* 1487 $[M + H]^+$. UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3

mol^{-1} cm^{-1}): 684 (3.5), 579 (4.8), 532 (sh), 296 (4.7) 241 (4.8) nm. IR (KBr): ν 803, 979, 1103, 1314, 1466, 1615, 1784, 2855, 2926, 2954 cm^{-1}. Anal. Calcd for $C_{72}H_{108}N_6S_6O_{12}BCl$: C, 58.11; H, 7.31; N, 5.65; S, 12.92. Found: C, 58.30; H, 7.14; N, 5.34; S, 12.73.

Chloro[2,3,9,10,16,17-hexa-*p*-tolylsulfonylsubphthalocyaninato]boron(III) (11). A solution of dry 1,2-dicyano-4,5-*p*-tolylsulfonylbenzene (**20**, 500 mg, 1.14 mmol) in anhydrous 1-chloronaphthalene (0.5 mL) was magnetically stirred at room temperature under argon atmosphere. Then 0.1 mL (1.14 mmol) of boron trichloride (previously condensed at −78 °C) was added through a cannula. The mixture was stirred at room temperature for 10 min. The reaction mixture was then heated at 140 °C during 30 min. After the mixture was cooled at room temperature, the solvent was removed by repeatedly washing with *n*-hexane. The residue was placed in the thimble of a Soxhlet extractor and extracted with chloroform. After the solvent was evaporated, the residue was washed with cold diethyl ether to yield 128 mg (25%) of subphthalocyanine **11** as a blue powder.

Mp: >250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.4 (s, 18H), 7.3 and 7.9 (AA′XX′ system, 24H), 8.9 (s, 6H) ppm. FAB-MS (3-NOBA): *m*/*z* 1354 [M$^+$], 1355 [M + H$^+$]. UV/vis ($CHCl_3$): λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 655 (3.8), 586 (4.6), 533 (sh), 313 nm (4.4). IR (KBr): ν 809, 1093, 1157, 1594, 2851, 2921 cm^{-1}. Anal. Calcd for $C_{56}H_{48}N_6S_6O_{12}BCl$: C, 48.19; H, 3.47; N, 6.02; S, 13.72. Found: C, 48.52; H, 3.21; N, 6.42; S, 14.01.

NLO Experimental Section. The permanent dipole moments in the ground state were experimentally obtained from capacitance measurements in chloroform solutions by a classical Guggenheim method.[37]

EFISH experiments have been performed in chloroform solutions, as a function of the concentration at two fundamental wavelengths, 1.907 and 1.34 μm. The shorter wavelength is directly emitted by a Q-switched Nd:YAG laser, whereas the longer one is obtained by Raman shifting the 1.064-μm emission of another Q-switched Nd:YAG laser in a high-pressure hydrogen cell (60 bar). A liquid cell with thick windows in the wedge configuration[38] was used to obtain a Maker fringes pattern. The incident beam was synchronized with a dc field applied to the solution in order to break its centrosymmetry.

HRS experiments were performed by measuring the intensity of the second-order scattered light on focusing an intense laser beam on the solution. The measurements were carried out at 1.46 μm to avoid the absorption bands at the harmonic signal and a possible multiphoton-induced fluorescence. In fact, the emitted light was spectrally analyzed to rule out this spurious contribution.

The experimental setup for the THG experiment at 1.34 μm is the same as the one used in EFISH experiments, but in this case without an external electric field.

No indications of any molecular degradation during the realization of the NLO experiments were observed.

Photophysical and Electrochemical Methods. Phenalenone (PN), 2-hydroxybenzophenone (2HBP), cresyl violet perchlorate (CVP), and propyl iodide were purchased from Aldrich. Tetrabutylammonium perchlorate (TBAP) was from Fluka. All were used as received. Spectroscopic grade benzene, methanol, and dichloromethane were from SDS. Dichloromethane was dried and columnated with basic alumina prior to use.

Absorption spectra were measured with a Varian Cary 4E spectrophotometer, periodically calibrated with a holmium oxide filter (Hellma). Fluorescence spectra were registered with a Shimadzu RF540. Fluorescence lifetimes were measured using an Edinburgh FL900 time-correlated single-photon-counting spectrometer. The laser setups for time-resolved $O_2(^1\Delta_g)$ near-IR phosphorescence detection (TPRD) and laser-induced optoacoustic calorimetry (LIOAC) have been described in detail elsewhere.[34] The system is based on a 5-ns pulsed nitrogen laser for excitation at 337 nm and uses a NorthCoast EO-817P germanium detector for TRPD and a 1-MHz piezoelectric ceramic transducer for LIOAC. The system has been expanded to accommodate a UV−vis transient absorption detection line, based on a 75-W Xe lamp and a red-sensitive Hammamatsu R928 photomultiplier coupled to a grating monochromator. Cyclic voltammograms were recorded using a three-electrode potentiostat, CAEM Instrumentation PGA 1210.

Fluorescence quantum yields were determined by comparing the area under the corrected spectra recorded for optically matched (±0.001 AU) solutions of the SubPcs in benzene and CVP in methanol ($\Phi_f = 0.54$),[39] exciting at 530 nm. Linearity in absorbance in the range 0.010−0.030 was carefully checked. The intensities were corrected for refraction index differences between methanol and benzene. No difference could be observed between air- and argon-saturated samples. Rate constants of fluorescence quenching by 1-iodopropane were determined by measuring the fluorescence intensity for several quencher concentrations. The absorbances of the SubPcs at the excitation wavelength were always smaller than 0.020. Singlet-state lifetimes were measured by the single-photon-counting technique in nitrogen-saturated benzene. Monoexponential decay kinetics were observed throughout.

The triplet-minus-singlet absorption coefficients were determined by transient absorption spectroscopy using the comparative method of Bensasson *et al.*[40] with benzophenone in benzene as reference ($\Phi_T\Delta\epsilon_{T-S} = 7220$ M^{-1} cm^{-1} at 525 nm).[41] The $\Phi_T\Delta\epsilon_{T-S}$ values obtained were combined with the Φ_T values determined by LIOAC to render the absorption coefficients. The methods used to determine Φ_T by LIOAC and Φ_Δ by TRPD are variations of the comparative method of Bensasson et al., described in detail elsewhere.[34] For LIOAC, 2-hydroxybenzophenone was used for calibration purposes, while for TRPD, phenalenone was the reference compound ($\Phi_\Delta = 0.95$).[34,42,43]

Cyclic voltammograms were recorded in the dark in a 10-mL cell. Dichloromethane solutions containing 0.1 M TBAP were purged with nitrogen for 20 min prior to the experiment. A cylindrical glassy carbon, a platinum wire, and a Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. The scan speed was set to 100 mV·s^{-1}.

Summary and Conclusions

Novel boron(III) subphthalocyanines (SubPcs) soluble in organic solvents containing a variety of donor and acceptor substituent groups have been synthesized by boron trihalide-induced cyclotrimerization of adequately substituted derivatives of phthalonitrile in 1-chloronaphthalene. For this purpose, we set out to synthesize phthalodinitriles equipped with iodo, nitro, alkyl- or arylthio, alkyl- or arylsulfonyl groups that are sufficiently stable under the required reaction conditions and also provide an easily accessible set of acceptor/donor substituents.

Their quadratic and cubic hyperpolarizabilities have been measured by EFISH (at two wavelengths), HRS, and THG to have a detailed assessment of their NLO response. β_{HRS} has been measured at 1.46 μm, where contamination from the multiphoton-induced fluorescence can be ruled out. β_{HRS} reaches high values that markedly depend on substitution. It shows a clear enhancement with the acceptor character of the substituents, the highest values being obtained for the strongest acceptor groups (**10** and **11**). They are comparable or even superior to many efficient second-order compounds. Much lower β values are obtained for the donor-substituted molecules, although the measurements are performed under more resonant conditions. A main outcome of these results is that an adequate choice of the substituents offers a promising route for optimization of the

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quadratic response of the SubPcs and confirms the high potential of these compounds for NLO applications. The cubic hyperpolarizabilities γ_{THG} show an opposite trend with substitution to that of β, possibly due to frequency dispersion effects. However, a quantitative analysis has not been possible due to the strong resonance with the B band.

The photophysical and electrochemical properties of this series of compounds have been determined and compared to those of their expanded analogues, the phthalocyanines. The compounds are strongly fluorescent, exhibit large intersystem-crossing quantum yields, sensitize the production of singlet oxygen with high efficiency, and are better photoreducing agents than phthalocyanines. These properties, combined with a remarkably lower tendency to aggregate owing to their cone-shaped geometry, make them candidates worthy of further studies for use in photosensitization and photoinduced electron-transfer processes.

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Supporting Information Available: ^{13}C NMR assignment for **8**, **9**, **10**, **13**, **14**, **19**, and **20**; absorption and fluorescence spectra of SubPcs **2**, **3**, **4**, **6**, **7**, **9**, and **11**; Stern−Volmer plots for **1**, **2**, **4**, **6**, **7**, **9**, and **11**; determination of Φ_{TET} by LIOAS; cyclic voltammograms of **1**, **2**, **4**, **6**, **7**, **9**, and **11**; triplet-minus-singlet absorption spectra of **1**, **3**, **4**, **6**, **7**, **9**, and **11**; and determination of F_D by TRPD for **1**, **3**, **4**, **6**, **7**, **9**, and **11** (40 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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