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Photophysical characterization of free-base corroles, promising chromophores for light energy conversion and singlet oxygen generation

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A detailed photophysical characterization of a series of six free-base corroles with different substitution patterns at *meso*-positions is presented. In air-free toluene at 295 K, the luminescence quantum yields range from 0.13 to 0.22 and lifetimes vary from 4.1 ns to 6.3 ns whereas in air-saturated toluene the lifetimes range from 3.8 ns to 5.6 ns. In glassy toluene at 77 K the lifetimes have values in the range 5.2 ns to 7.9 ns. Transient absorption spectra of the singlet excited states have positive bands art $\lambda < 550$ nm and at $\lambda >$ 680–700 nm. The transient absorption spectra of the lowest triplet display a band around 460–470 nm and bleaching features in the Q bands region, no absorption above 700 nm. The triplet lifetimes in air-free toluene are in the interval 50–150 μs. The lowest excited states react with oxygen and sensitized singlet oxygen ($^1\Delta_g$) yields of 0.51–0.77 are determined *via* its luminescence. Electron and energy transfer from the excited states to molecular oxygen is discussed. Effect of polar solvents on the luminescence parameters indicate that charge transfer (CT) excited states play a very minor role. Thermal and photo stability is excellent for most of the examined compounds in toluene and dichloromethane.

Introduction

Corroles are synthetic aromatic macrocycles of the tetrapyrrolic family, that also includes porphyrins, phthalocyanines and corrins. They possess the same skeleton of corrins (only three meso carbons between the four pyrrole rings) but with a fully conjugated macrocycle like porphyrins. The first syntheses of corroles were reported in 1965[1] but research activity has remained low for decades,[2] until recently synthetic breakthroughs[3,4] and subsequent developments[5] made these compounds readily available. In more recent years the interest in these compounds has grown[6] as has the number of applications, which span from antitumor therapeutic properties[7] to catalytic[8] and important sensor applications.[9,10]

The spectroscopic properties—absorption and luminescence—have been studied in some detail and have shown very interesting features.[11–14] Free base and metalated corroles display strong absorption bands ($\varepsilon = 120\,000$ M^{-1} cm^{-1}) in the high energy side of the visible spectra and moderate absorption bands around 500–650 nm ($\varepsilon = 10\,000/20\,000$ M^{-1} cm^{-1}), called respectively Soret and Q bands in analogy to porphyrins. Luminescence properties have also proven to be very promising: the lowest excited singlet state with a few nanoseconds lifetime and an energy of *ca.* 2 eV displays a high luminescence quantum yield, of the order of 0.2–0.7, considerably higher than that of closely related porphyrins. Whereas several theoretical studies providing a rationale for the interpretation of the low energy transitions have appeared,[15–18] no dedicated paper addressing in detail the different aspects of the photophysics of these compounds has been published so far.[19] The electrochemistry and spectro-electrochemistry of corroles have also been investigated, showing, in brief, that corroles are easier to oxidize and more difficult to reduce than porphyrins and that the corrole cations have a distinct, red shifted spectrum with respect to the ground state.[20–21]

The above spectral and electrochemical properties, which exhibit several similarities but also distinct features with respect to the more used porphyrin analogues, make corroles promising candidates as building units of photo- and electroactive multi-component arrays. In particular, our interest is to establish whether these relatively new chromophores can be conveniently used for the construction of arrays where light absorption can trigger some useful function, either photoinduced energy and/or electron transfer. Several corrole–corrole or porphyrin–corrole dyads have been reported so far,[22–24] but—to our knowledge—there is only one report on a corrole containing molecular dyad designed to achieve photoinduced processes.[11a] Unfortunately, the porphyrin–corrole dyad designed to perform vectorial energy transfer displayed photoinstability leading to the corresponding porphyrin–biliverdin species. Photo stability of the corroles and their assemblies is a rather critical issue when the aim is that of using these molecules for light energy conversion.

We present here a detailed photophysical study of a series of six free-base corroles, providing a spectroscopic characterization of their excited states and of their reactivity under different experimental conditions. In the course of the experiments we also paid attention to photo and thermal stability which is also briefly commented in this report. The series of free-base *meso*-triarylcorroles **1–6** examined (Chart 1) contains a simple prototype 5,10,15-triphenylcorrole (**6**) and four corroles (**1–5**) bearing additional groups (CF_3, F, CH_3 or CN) at the *meso* phenyls.

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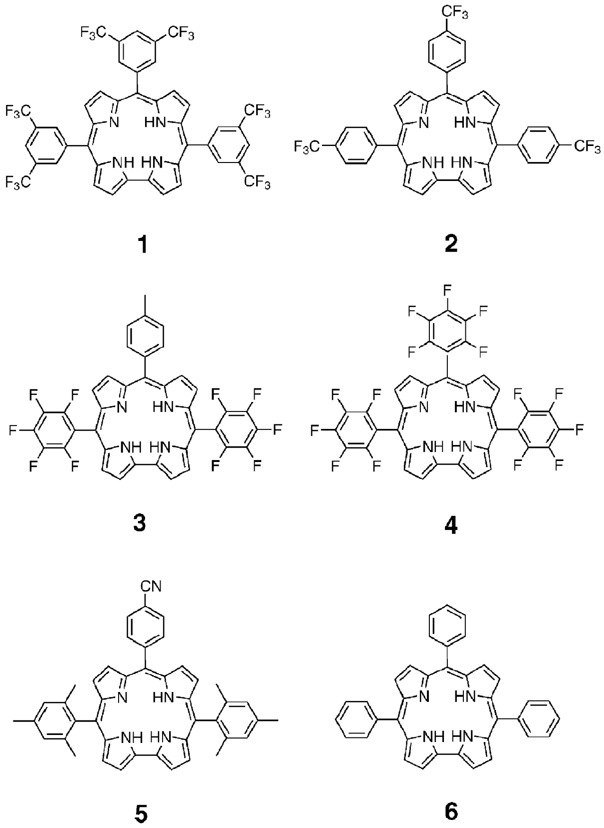

Chart 1

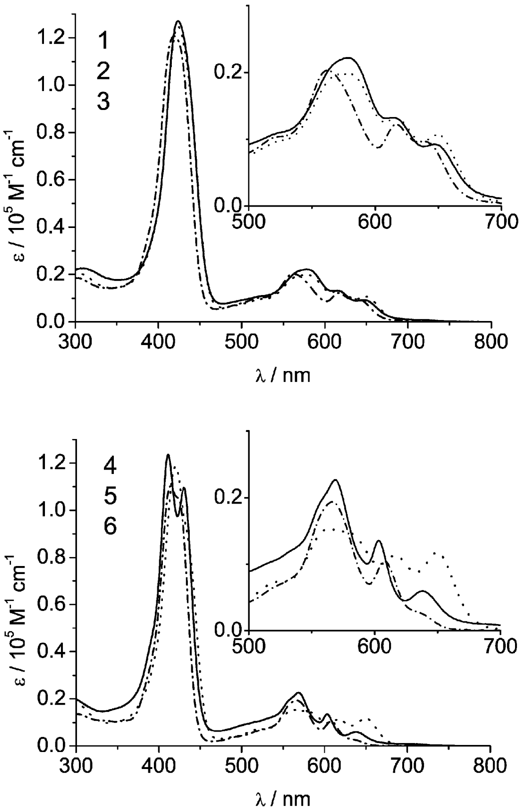

Fig. 1 Absorption spectra of corroles in aerated toluene solutions at room temperature. Upper panel: **1** (solid line), **2** (dotted line), **3** (dashed-dotted line). Lower panel: **4** (dashed-dotted line), **5** (solid line) and **6** (dotted line).

Results and discussion

Steady-state spectroscopy

The absorption spectra of corroles **1–6** in toluene are shown in Fig. 1 and epsilon values are collected in Table 1. Previous work has shown that the porphyrin "four-orbital model" holds well for corroles.[15] All the examined corroles, in fact, exhibit typical Soret-type bands with $\lambda_{\max}$ around 420 nm, and Q-type absorption bands in the region 500–650 nm. With respect to more symmetrical porphyrins, in corroles the number of bands is increased because of the reduced symmetry. The position of Soret absorption maxima is not very sensitive to the nature of the *meso* subsituents (Table 1), as previously reported,[25,26] but a clear splitting is detected for corrole **5** containing two mesityl substituents at the *meso* position, in agreement with previous observations.[27] The most likely reason for the splitting of the Soret band in **5** could be a deviation from planarity of the macrocycle induced by the bulky mesityl substituents, in analogy with the behavior of a corrole exhibiting an important steric hindrance at the periphery of the macrocycles due to ethyl substituents at the β positions of the pyrroles.[11b] The Q bands present a more complex pattern. It is known, in fact, that the b_1 HOMO orbital of corroles, like the a_{2u} HOMO orbital in porphyrins, places considerable charge on the *meso* carbons;[15] shift of this level by *meso*-substitution can thus affect the relative Q transitions. A detailed discussion on the effect of the substituents is however beyond the aim of the present study. The molar absorption coefficients values of the examined corroles in toluene (Table 1) are in agreement with previous reports.[11–15]

Corrected emission spectra of optically matched solutions of corroles **1–6** in de-aerated toluene at room temperature upon excitation at 550 nm are displayed in Fig. 2. By analogy with free-base porphyrins the luminescence bands detected for each corrole can be attributed to a vibrational progression of the lowest singlet excited state. The luminescence of corroles **1** and **2** occurs at the same wavelength as the luminescence of the unsubstituted triphenylcorrole **6** (bands at 670 and 710 nm approximately), whereas the emission of corroles **3**, **4** and **5** is blue-shifted (see Table 2). In particular the luminescence of corrole **4** with three fully fluorinated benzene rings at the *meso* positions is the most hypsochromically shifted (bands at 645 and 707), in agreement with data reported in previous studies.[12,13,19] The five free-base corroles have fluorescence quantum yields that range from 0.13 to 0.22 (Table 2), considerably higher than those of free-base porphyrins, [28,29] and in agreement with previous reports.[13,14] Some inconsistency with the emission quantum yields previously reported by Paolesse *et al.* could be ascribed to the use by this group of a different standard for luminescence quantum yields.[11b] Corrole **2** and **6** present the highest fluorescence quantum yields whereas the lowest yield (0.13) is exhibited by corrole **4** that has three fully fluorinated benzene rings.

Excitation spectra of corroles **1–6**, detected on the maximum of the two emission bands for each corrole, show a good agreement with absorption spectra in all cases, indicating a genuine emission ascribable to corroles. As an example the excitation spectrum of **1** and **5** is reported in Fig. 3 together with the pertinent absorption spectrum arbitrary scaled. The comparison between absorption and emission spectra reveals a good mirror image with a modest Stokes shift, in agreement with a very low degree of distortion of the emitting excited states. Fig. 4 shows the non-corrected emission spectra at room temperature in toluene, reported along with their low energy absorption bands arbitrary scaled for corroles **1** and **6**.

It should be noticed that upon excitation on the Soret band, the emission quantum yields are essentially the same, within experimental error, to those detected for excitation on the Q bands (Table 2). This indicates that the internal conversion from the S_2 state is fast, setting for the lifetime of this state an

Table 1 Molar absorption coefficient of **1–6** in aerated toluene solutions at room temperature

	$\lambda_{\max}$/nm	$\varepsilon/10^5\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$
1	423	1.27
	525 (sh)	0.11
	568 (sh)	0.21
	578	0.22
	616	0.13
	647	0.09
2	423	1.25
	524 (sh)	0.10
	578	0.20
	616	0.13
	650	0.11
3	419	1.21
	523 (sh)	0.10
	562	0.20
	617	0.12
	640	0.10
4	414	1.10
	424 (sh)	1.05
	518 (sh)	0.06
	566	0.19
	608	0.10
	634 (sh)	0.03
5	411	1.24
	430	1.09
	556 (sh)	0.19
	569	0.23
	603	0.14
	638	0.06
6	420	1.19
	523	0.07
	562	0.15
	579 (sh)	0.15
	616	0.11
	650	0.12

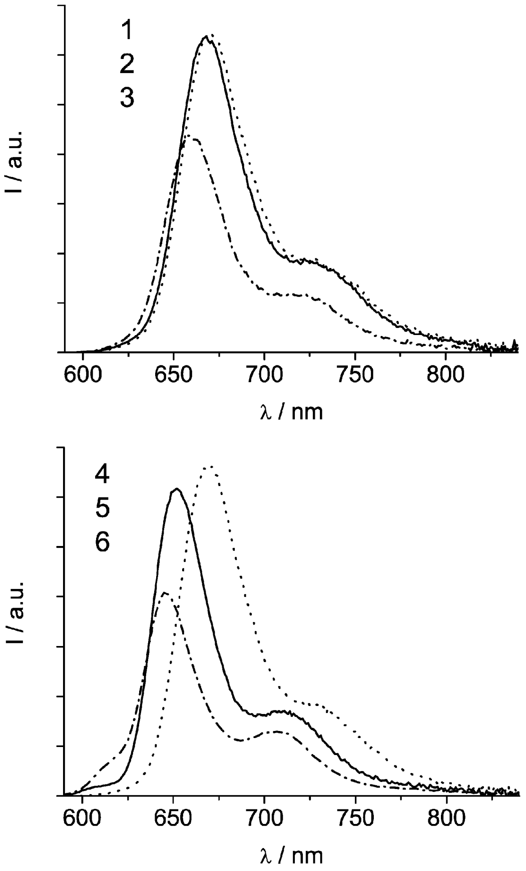

Fig. 2 Corrected emission spectra of optically matched solutions (A = 0.138) excited at 550 nm. Upper panel: **1** (solid line), **2** (dotted line), **3** (dashed-dotted line). Lower panel: **4** (dashed-dotted line), **5** (solid line) and **6** (dotted line).

upper lifetime value of few picoseconds, as occurs for porphyrins.[30]

The emission spectra of corroles **1–6** in glassy toluene solution at 77 K are collected in Table 2. The fluorescence band maxima shift to slightly lower wavelength with respect to 295 K data indicating a modest effect of the solvent rigidity on the stabilization of the excited state, and the bands become narrower with respect to room temperature as occurs with spectra registered in solid matrices.[31] The energy levels of the emitting states are derived from the corrected high energy emission maxima at 77 K and appear in Table 2. No phosphorescence could be detected for any examined corrole in the visible and near IR range even by making use of halogen-containing solvents (1,1,2,2-tetrabromoethane or diiodomethane) which are known to favor intersystem crossing by the external heavy atom effect. By analogy to porphyrins the triplet is expected to have an energy of *ca.* 1.4–1.5 eV, which would place the phosphorescence band around 800–900 nm. The fact that no luminescence could be detected can point to a reduced intersystem crossing efficiency from singlet to triplet excited states compared to free-base porphyrins, which is in agreement with the noticed increase in fluorescence quantum yields. However we can anticipate that the triplet could be easily identified even at ambient temperature by its transient absorption making use of the laser-flash-photolysis technique (see below).

Time resolved spectroscopy

The fluorescence lifetimes at room temperature in air-free and in air-equilibrated toluene solutions of **1–6**, determined both

Table 2 Fluorescence data of corroles **1–6** in toluene at 295 K and in rigid toluene glass at 77 K

	295 K					77 K		
	$\lambda_{\max}{}^{a}$/nm	$\Phi_{\mathrm{fl}}{}^{b}$	$\Phi_{\mathrm{fl}}{}^{c}$	τ^{d}/ns	$k_{\mathrm{r}}{}^{e}/\mathrm{s}^{-1}$	$\lambda_{\max}{}^{a}$/nm	τ/ns	E^{f}/eV
1	668, 725	0.21	0.20	5.7 (5.0)	3.7×10^7	656, 726	6.1	1.89
2	670, 730	0.22	0.20	5.2 (4.7)	4.2×10^7	663, 732	5.5	1.87
3	659, 720	0.14	0.14	4.1 (3.8)	3.4×10^7	654, 722	5.2	1.90
4	645, 707	0.13	0.13	4.8 (4.3)	2.7×10^7	642, 705	6.1	1.93
5	652, 710	0.19	0.18	6.3 (5.6)	3.0×10^7	644, 706	7.9	1.93
6	669, 730	0.22	0.21	4.8 (4.3)	4.6×10^7	666, 730	5.5	1.86

[a] $\lambda_{\max}$ for the two bands derived from corrected emission spectra. [b] Luminescence quantum yields in air-free toluene, determined comparing corrected emission spectra and using TPP (tetraphenylporhyrin) in aerated toluene as a standard ($\Phi_{\mathrm{fl}} = 0.11$[28]). Excitation at 550 nm. [c] As [b] but excitation is at 460 nm. [d] Fluorescence lifetimes in air-free toluene, air equilibrated toluene in parenthesis. Excitation at 373 nm. [e] Radiative rate constants. [f] Derived from the emission maxima at 77 K.

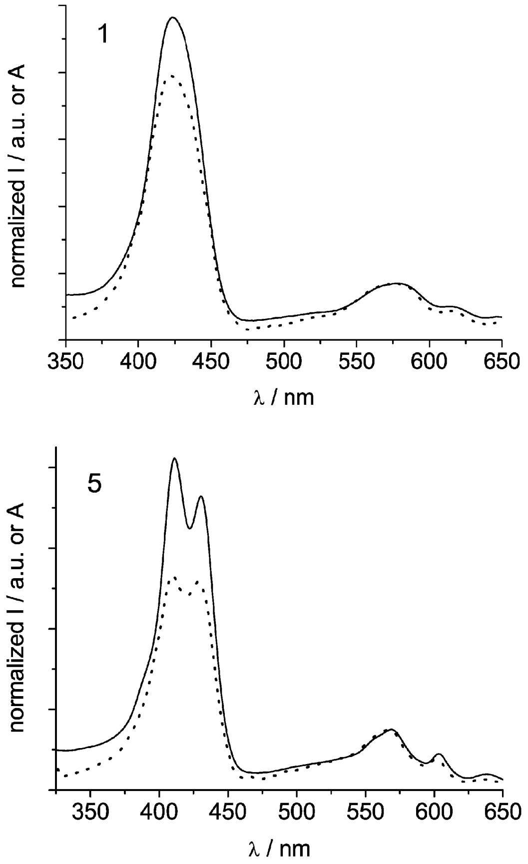

Fig. 3 Normalized excitation spectra in toluene solutions at 295 K and absorption spectra of: (upper) **1**, $\lambda_{em} = 668$ nm (dotted line) and absorption (full line), (lower) **5**, $\lambda_{em} = 652$ nm (dotted line) and absorption (full line). Excitation spectra read on the emission band around 715 nm gave identical results.

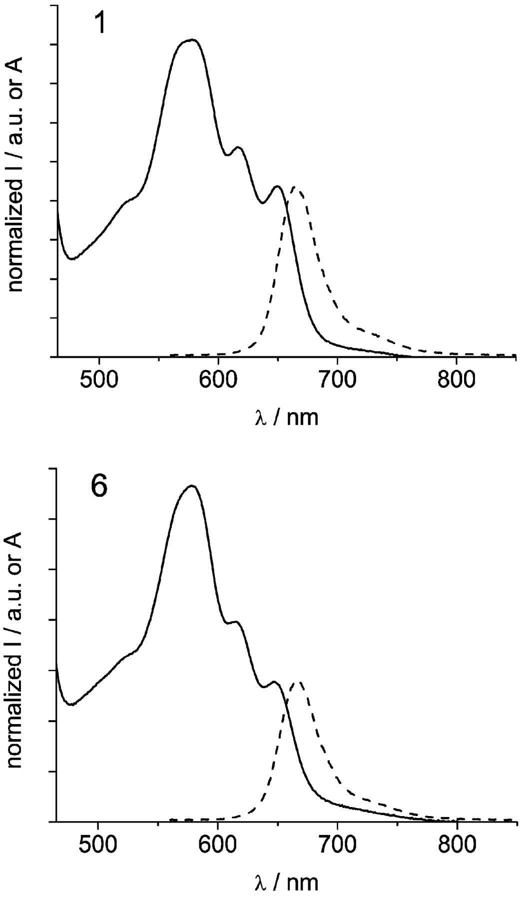

Fig. 4 Absorption spectra in the low energy transition bands (full line) overlapped with normalized emission spectra (dashed line) for corrole **1** (upper) and corrole **6** (lower).

on the 650–670 nm band and on the 710–730 nm shoulder are identical and appear in Table 2. In de-aerated solutions the lifetimes are in the range of 4.1–6.3 nanoseconds and they are reduced by *ca.* 10–15% in aerated solutions, indicating a very high reaction rate of the excited state with oxygen (see below). The fluorescence lifetimes in glassy solutions at 77 K (Table 2) display only a modest increase, indicating that excited singlet decay is essentially an activationless process. Table 2 collects all the data related to luminescence and allow to calculate the radiative rate constant k_r($k_r = \Phi_{fl}/\tau$) which is of the order of 3–4 × 10^7 s^{-1} for all corroles, similar to that of porphyrins which is of the order of *ca.* 2 × 10^7 s^{-1}.[30]

The singlet excited state can be characterized also by its absorption spectrum; in Fig. 5 are reported the spectra measured after excitation at 532 nm by a picosecond laser system for corroles **2** and **3** in air-equilibrated toluene, as an example. The spectrum of the singlet is similar for all corroles and is characterized by two positive bands, one more intense extending around or below 500 nm, and the other occurring around 700 nm and extending toward the infrared region of the spectrum. The region from 550 to 650 is dominated by the bleaching features of the ground state whereas the region from 650 nm to 700 nm is dominated by the stimulated emission; both features are characterized by an increase of transmittance *i.e.* a negative value in the absorbance graph. The ground state absorption and the emission bands are also reproduced in the upper graph of Fig. 5 to help the reader in the identification of the various contributions to the overall spectrum. The spectra are taken every 660 ps after the end of the pulse and the time window of the experiment is *ca.* 3.3 ns, during which the evolution from the singlet (spectrum at time zero) to the triplet (spectrum at 3.3 ns) can be appreciated to some extent. The conversion is far from complete since the lifetimes of the species are respectively 4.7 ns for **2** and 3.8 ns for **3**. The lifetime which can be calculated for the decay of the spectrum (insets of Fig. 5) is, in spite of the reduced time window, perfectly consistent with the lifetimes measured by luminescence, confirming the identity of the detected species.

The final spectrum detected in the picosecond experiment at 3.3 ns already contains some triplet contribution, but the long lived triplet state can be better probed by a nanosecond flash-photolysis system. The transient absorption spectra obtained at ambient temperature in air-free toluene solutions at the end of the laser pulse and after 50, 100, 150 μs are shown in Fig. 6 for **2** and **4**. The spectra, very similar for all corroles, are dominated by a strong absorption band around 470 nm and by the bleaching features of the ground state up to 650 nm; at variance with the singlet excited state no absorbance is displayed above 660–700 nm. The spectral features are reported in Table 3 with the lifetimes in air-free and air-equilibrated toluene solutions. The triplet lifetimes in air-free solutions are of the order of 50–150 μs and exhibit a large effect of the substituents. Their value is very different from a 870 μs lifetime in air-free toluene at room temperature previously reported for corrole **4**,[12] but the apparent discrepancy could be due to the more effective air purging method used by the other group.[32]

Reactivity with oxygen

Both singlet and triplet excited states of corrole are highly reactive with ground state molecular oxygen; Table 4 collects the reaction rates calculated from the experimental data.[33] The mechanism of quenching could be due either to energy transfer, or to electron transfer, yielding respectively singlet oxygen $^1\Delta_g$ ($E_{0-0} = 0.98$ eV), or superoxide ion, O_2^-. In principle, the energy stored in the singlet excited states of the present

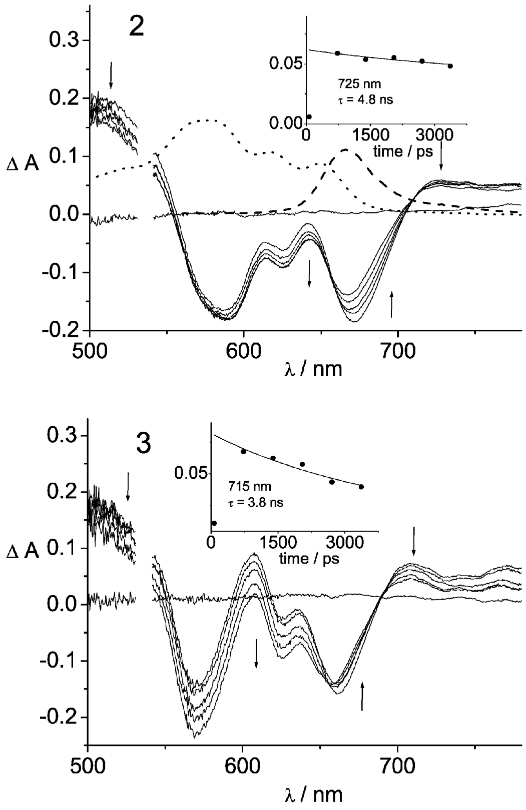

Fig. 5 Transient absorbance detected in air-saturated toluene solutions of corrole **2** (A_{532} = 0.45) and **3** (A_{532} = 0.67) after excitation with 532 nm light (35 ps pulse, 3 mJ per pulse): spectra taken in the interval 0–3.3 ns after the pulse at time steps of 660 ps. In the upper panel the arbitrary scaled absorption spectrum (dotted line) of the ground state and the emission of **2** (dashed line) are displayed. The decay kinetics of the singlet excited state are reported in the insets.

corroles, *ca.* 1.9 eV, would be sufficient to promote electron transfer from corroles to oxygen. The reduction potential of O_2 is in fact of the order of −0.8 V (*vs* SCE) and the present corroles can be oxidized at *ca.* 0.6–0.8 V.[20b,34] On the contrary, electron transfer from triplet state, if we assume a reasonable value of the triplet energy of the order of 1.5 eV (see above), would not be thermodynamically allowed. Singlet oxygen was formed in toluene solutions of all corroles after excitation at λ = 550 nm, as testified by detection of the typical luminescence band of singlet oxygen with maximum at 1268 nm, displayed for some representative cases and the reference 5,10,15,20-tetraphenylporphyrin (TPP) in Fig. 7.[35] In Table 4 are collected the yields of $^1\Delta_g$ production and the redox potentials of corroles **1–6**. The rate constants for reaction of oxygen with the singlet excited states are of the order of 1.2×10^{10} M^{-1} s^{-1}, corresponding to the diffusion limit in toluene (1.1×10^{10} M^{-1} s^{-1} at 293 K[36a]) whereas those with the triplets are around 3×10^9 s^{-1}, very similar to the reaction rate of oxygen with porphyrin triplets.[36b] The yield of $^1\Delta_g$ vary by *ca.* 35% within the series. This could obviously depend on remarkably different triplet yields for the corroles **1–6**, but it is not justified by the radiative rate constants k_r of Table 2 which seem to indicate a rather homogeneous behavior. On the contrary, there is a clear correlation between lower yield of singlet oxygen $^1\Delta_g$ and more facile oxidation of the corrole (Table 4), which suggests that electron transfer from the singlet excited state can compete with energy transfer in these compounds. Electron transfer rate is expected to increase when the driving force of the electron transfer reaction increases, *i.e.* when the redox potential of the donor decreases, and would better compete with the energy transfer. This would result in a decrease of sensitized singlet oxygen yield. Unfortunately a direct detection of the O_2^- species is biased by its low molar absorption coefficient,

Table 3 Triplet excited state spectral features and lifetimes in toluene solutions at 295 K

	λ_{max}/nm	τ^a/μs	τ^b/ns
1	470	65	184
2	470	74	205
3	460	136	209
4	460	150	246
5	460	73	242
6	470	55	150

[a] Air-free solutions. [b] Air equilibrated solutions.

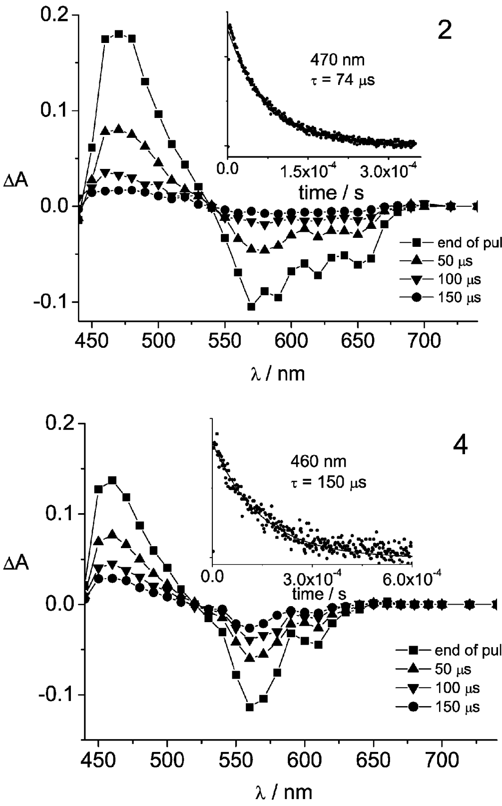

Fig. 6 Transient absorption difference spectra for corroles **2** (upper, A_{532} = 0.39) and **4** (lower, A_{532} = 0.26) in air-free toluene solutions obtained at various delay times (0–150 μs), after excitation at 532 nm (18 ns pulse, 1.4 mJ per pulse). Insets show the time decay observed at the indicated wavelength determined at *ca.* 0.1 mJ per pulse (see experimental section).

Table 4 Reaction rates with oxygen of excited states and singlet oxygen ($^1\Delta_g$) luminescence yields in toluene, 295 K. In the last column are redox potentials

	Singlet k_q/M^{-1} s^{-1}	Triplet k_q/M^{-1} s^{-1}	$\Phi_\Delta{}^a$	Redox Potentials^b/Volts
1	1.4×10^{10}	3.0×10^9	0.64	+0.72
2	1.1×10^{10}	2.7×10^9	0.61	+0.58
3	1.1×10^{10}	2.7×10^9	0.77	+0.87^c
4	1.4×10^{10}	2.3×10^9	0.71	+0.87
5	1.1×10^{10}	2.3×10^9	0.52	+0.56
6	1.3×10^{10}	3.7×10^9	0.51	+0.42^d

[a] Emission quantum yield, the standard used is TPP in aerated toluene at room temperature (ϕ_Δ = 0.70 [35]). [b] Half-wave potentials for first oxidation of corroles in benzonitrile from ref. 20*b*. [c] Value for the similar compound **4**. [d] Value for similar 5,10,15-tris(4-methylphenyl)-corrole.

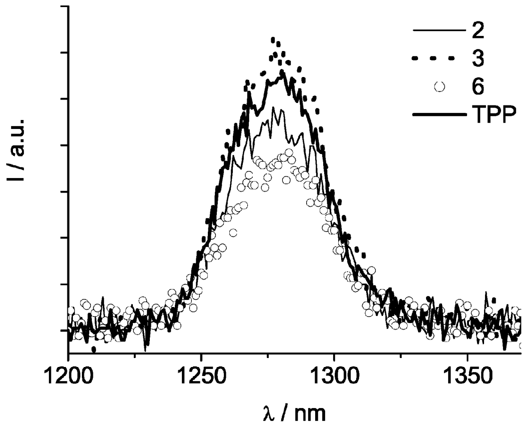

Fig. 7 Singlet oxygen luminescence detected in air-equilibrated toluene after excitation at 550 nm for optically matched solutions of **2**, **3**, **6** and TPP in toluene.

ca. 2000 M^{-1} cm^{-1}, and by the far UV region of its absorption, $\lambda_{max} = 240$ nm.[37]

Solvent effect on photophysical parameters

The experiments reported so far have been carried out in toluene (dielectric constant 2.4); in order to have some further insight into the nature of the excited states we repeated some experiments on a selected number of corroles in solvents of increasing polarity, namely dichloromethane (dielectric constant 8.9) and benzonitrile (dielectric constant 25.9). The selected corroles were **2**, **3** and **6**, since **6** can be considered a prototype for the meso triaryl substitution, **2** is representative of the CF_3 phenyl substitution pattern and **3** is representative of the fluorinated phenyl pattern. In Fig. 8 are reported the absorption spectra in the three solvents, and in Table 5 are collected the photophysical parameters in the two new solvents, to be compared with Table 2 for toluene. Solvents polarity affects only slightly the absorption spectra; a common feature seems to be a shift to higher energy of the Soret band in dichloromethane. Luminescence properties appear more interesting: whereas the data of corrole **2** and **6** are rather erratic and it is difficult to find a straightforward trend, a clear trend can be observed for corrole **3**. In passing from toluene to dichloromethane and from the latter to benzonitrile there is a progressive blue shift of the emission maxima, an increase of the fluorescence quantum yield, a decrease of the lifetime and a consequent increase of the radiative rate constant that reaches the maximum value observed among all corroles in the different solvents (6.7×10^7 s^{-1}). These data support the hypothesis that the ground state of **3** is more stabilized than its lowest singlet excited state by the increased polarity of the solvent, which indicates an excited state in **3** with a reduced dipole moment with respect to the ground state.

Remarkably, for all examined compounds the excitation on the Soret band leads to a very low emission quantum yield when dichloromethane is used as a solvent. This solvent seems to introduce a deactivation pathway which is not present in the other two solvents and could be related to the typical acidity of this solvent. It has to be noticed that the reaction rate with oxygen in dichloromethane (*ca.* 8×10^9 M^{-1} s^{-1}) and in benzonitrile (*ca.* 5×10^9 M^{-1} s^{-1}) is lower than in toluene (1.2×10^{10} M^{-1} s^{-1}). Whereas in the case of benzonitrile this could simply be assigned to a reduced diffusion rate in this solvent, which is of the order of 5×10^9 M^{-1} s^{-1},[38] in the case of dicloromethane the rate is about half the diffusional one, *i.e.*

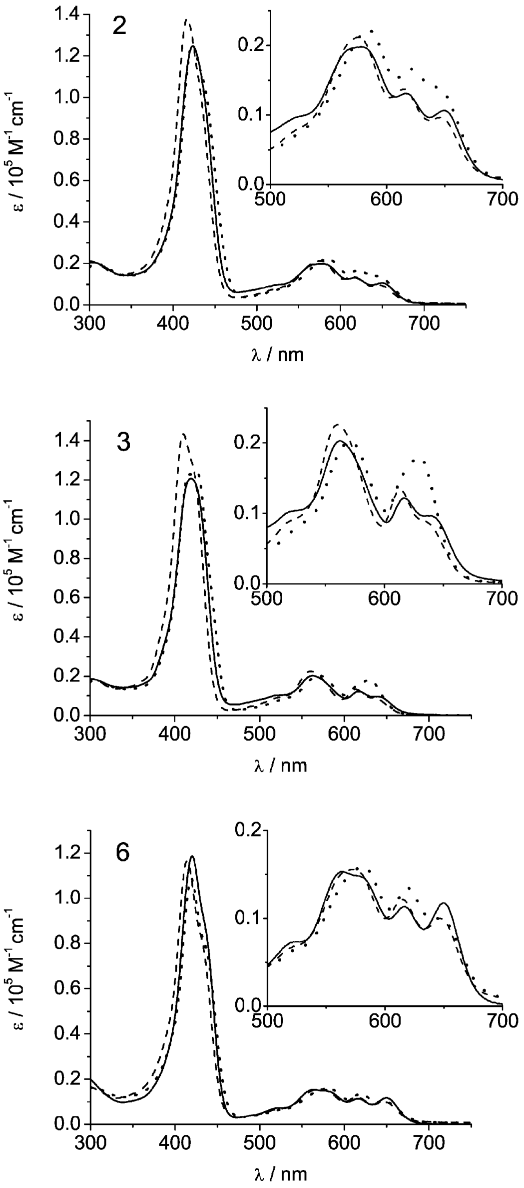

Fig. 8 Ground state absorption spectra of **2**, **3** and **6** in toluene (solid line), dichloromethane (dashed line) and benzonitrile (dotted line) at room temperature.

Table 5 Fluorescence data of corroles **2**, **3** and **6** in dichloromethane and benzonitrile (λ_{max} derived from corrected emission spectra)

	Dichloromethane						Benzonitrile					
	λ_{max}/nm	Φ_{fl}[a]	Φ_{fl}[b]	τ[c]/ns	k_r[d]/s^{-1}	k_q[e]/M^{-1} s^{-1}	λ_{max}/nm	Φ_{fl}[a]	Φ_{fl}[b]	τ[c]/ns	k_r[d]/s^{-1}	k_q[e]/M^{-1} s^{-1}
2	664	0.20	0.12	4.2 (4.0)	4.8×10^7	5.4×10^9	668	0.19	0.18	4.5 (4.2)	4.2×10^7	8.4×10^9
3	654	0.17	0.09	3.8 (3.5)	4.5×10^7	1.0×10^{10}	650	0.24	0.25	3.6 (3.5)	6.7×10^7	—
6	664	0.16	0.05	3.8 (3.6)	4.2×10^7	6.6×10^9	670	0.20	0.13	4.2 (4.1)	4.8×10^7	3.1×10^9

[a] Emission quantum yield, excitation at 550 nm. [b] Same as[a] but excitation at 460 nm or 455 nm. [c] Fluorescence lifetimes in air-free solutions, in parenthesis is the lifetime in air-equilibrated solutions. Excitation at 373 nm. [d] Radiative rate constants. [e] Reaction rate of singlet excited state with oxygen, calculated from solubility data of ref. 33.

1.5×10^{10} M^{-1} s^{-1}.[36a] For the latter case the reduced rate in oxygen quenching could be due to the effect of polarity on the electron transfer rate, which we have hypothesized to be an important path in the quenching of singlet excited states of corroles by oxygen (see above). The effect of solvent polarity should play a role both on the stabilization of the encounter complex and on the stabilization of the electron transfer products but a detailed analysis of this effect, which would require further investigations, is beyond the aim of the present study.

Thermal and photochemical stability

Thermal and photochemical stability in toluene was tested for all corroles whereas in benzonitrile and dichloromethane only the stability of selected corroles **2**, **3** and **6** was examined.

Corroles **1–6** showed an excellent thermal stability in toluene solutions. A good thermal stability was also displayed by **2**, **3**, and **6** in dichloromethane and benzonitrile after 24 hours in the dark. As regards the photostability in toluene, only corroles **5** and **6** were found to be unstable: after a few minutes of laser irradiation the absorbance decreased by about 20–30% and a new band centered around 710–730 nm appeared. Of the three examined corroles (**2**, **3**, **6**), in dichloromethane **2** and **3** were photo-stable, but all were photo-labile in benzonitrile. In summary corroles **1–6** showed a good thermal stability in all the examined solvents and most of them displayed a good photochemical stability in toluene and dichloromethane. All these observations as well as the fact that photostability strongly increases when electron-withdrawing substituents are present around corrole periphery are in excellent agreement with previous findings.[39,40] The type of change brought about by light irradiation appears to be in most cases the same, with the formation of a product with a maximum of absorption around 710–730 nm which could perhaps be assigned to biliverdin as already observed in previous cases.[11a]

Conclusions

A series of free-base corroles with different substitution patterns has been spectroscopically and photophysically characterized in toluene solutions. The singlet excited states display high fluorescence quantum yield, lifetime in the order of few nanoseconds, characteristic absorption features above 680 nm different both from the ground state and from the triplet excited state. Reaction with oxygen is fast and the quenching is assigned in part to electron transfer. The triplet states display an intense absorption spectrum without any spectral feature above 700 nm, with lifetimes of the order of one hundred microseconds and react with O_2 to yield singlet oxygen $^1\Delta_g$. The effect of solvent polarity on the photophysical parameters has been tested to ascertain the role of excited states with charge transfer characters: the data clearly indicate that this type of excited states has no relevance in the present case. Photo- and thermal-stability tests have shown that most of the examined corroles are remarkably stable in toluene and dichloromethane. This feature together with the spectral, the electrochemical and the photophysical properties makes these compounds promising building blocks for the assembly of photo-active arrays to be used in the conversion of light into chemical energy. The high yield of singlet oxygen sensitization of these chromophores, reported here for the first time, can open promising applications.

Experimental

The synthesis of the corroles **1–2**,[41] **3**,[39] **4**,[41] **5**,[42] and **6**[41] has been reported elsewhere. The solvents used were spectroscopic grade toluene (C. Erba), spectroscopic grade dichloromethane (C. Erba), HPLC grade benzonitrile (SIGMA-Aldrich), 1,1,2,2-tetrabromoethane (Analyticals RPE), and diiodomethane (Analyticals RPE). Diiodomethane was chromatographically purified on silica-gel. Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer and emission spectra, corrected for the photomultiplier response, were detected by a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier. 5,10,15,20-Tetraphenylporphyrin (TPP) in aerated toluene was used as a standard with $\Phi_{fl} = 0.11$.[28] Experiments at 77 K made use of quartz capillary tubes immersed in liquid nitrogen contained in a home-made quartz Dewar. Attempts to detect phosphorescence were performed with the Spex Fluorolog II spectrofluorimeter equipped with a phosphorimeter accessory (1934D, Spex). The near IR emission (range 800–1500 nm) was probed with an FLS920 spectrofluorimeter (Edinburgh) equipped with an Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with a NIR grating blazed at 1000 nm. The latter spectrofluorimeter was also used to measure the singlet oxygen luminescence quantum yield against the ϕ_Δ from TPP in toluene as reference ($\Phi_\Delta = 0.70$[35]).

Fluorescence lifetimes in the nanosecond range were detected by a Time Correlated Single Photon Counting apparatus (IBH) with excitation at 373 nm.

Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd-YAG laser (Continuum PY62/10, 35 ps pulse). The second harmonic (532 nm) at a frequency of 10 Hz and an energy of *ca.* 3 mJ per pulse was used to excite the samples whose absorbance at the excitation wavelength was *ca.* 0.5. The residual 1064 nm light (*ca.* 40 mJ) was focused on a stirred 10 cm cell containing a mixture of D_2O/D_3PO_4 to produce a white light continuum which was used as analyzing light. A computer-controlled optical delay stage (Ealing) on the path of the excitation beam provided a delay between excitation and analysis. The analyzing light was split in two parts probing respectively irradiated and unirradiated portions of the sample and crossed the sample cell in a nearly collinear geometry with respect to the excitation beam. The transmitted probes were fed *via* optical fibers into a spectrograph (Spectrapro 275, Acton) and were detected in two separate regions of a CCD detector (Princeton Instruments). Spectra at increasing time delays between the pump and the probe were acquired by a customized software (Eurins) and typically 500 laser shots were collected and averaged to get a single spectrum at a specific time delay. Kinetic analyses were made by selecting the absorbance values of successive time resolved spectra at the selected wavelength and by applying standard iterative procedures. More details can be found elsewhere.[43]

Transient absorbance in the nanosecond range made use of a laser flash photolysis apparatus based on a Nd:YAG laser (JK Lasers) delivering pulses of 18 ns. The second harmonic was used for excitation. Absorbance of the solutions at the exciting wavelength was *ca.* 0.3 and the energy used was of 1.4 mJ per pulse for the determination of the spectra and *ca.* 0.1 mJ per pulse for the triplet lifetime determination, in order to prevent undesired second order T–T annihilation reactions. For more details see previous reports.[44] Experiments were conducted in home made, 10 mm optical path cuvettes, bubbled with argon for 10 minutes and sealed.

All the stability experiments were carried out with concentrations of the order of 1×10^{-5} M at 295 K.

Estimated errors are 10% on transient absorbance lifetimes, 8% for luminescence lifetimes, 10% for molar absorption coefficients and 20% on quantum yields and working temperature, if not otherwise specified, was 295 ± 2 K.

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