Photophysical and photosensitizing properties of brominated porphycenes†

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A heavy atom, bromine, was directly substituted into the porphycene macrocycle to promote intersystem crossing by way of spin–orbit coupling. The singlet oxygen production ability of the porphycene is dramatically enhanced, and the highest value of 0.95 for the quantum yield of singlet oxygen generation (Φ_Δ) was obtained for the dibrominated porphycene by visible light excitation.

Inspired by the significance of the porphyrins, a new research direction has emerged devoted to the preparation and study of non-porphyrin tetrapyrrolic macrocycles.[1] Among them, porphycene, a structural isomer of porphyrin, was first synthesized by Vogel and co-workers in 1986.[2] This isomer exhibits geometries of the N_4 core which deviate from the ideal square shape of the porphyrin core, resulting in an interesting electronic structure of the porphycene.[3] For example, porphycenes show a higher absorption than porphyrins in the red spectral region due to the lower molecular symmetry.[3] Therefore, porphycenes are excellent candidates as photosensitizers.[4] In particular, the photosensitized production of singlet oxygen has significance in the areas of photo-oxidation, DNA damage, and photodynamic therapy of cancer.[5] The singlet oxygen generating ability of a photosensitizer is measured by its quantum yield (Φ_Δ). Vogel reported a Φ_Δ value of 0.36 for 2,7,12,17-tetra-*n*-propylporphycene (**1**).[6] This value is not very high compared to those for other sensitizers including porphyrins.[7] Therefore, our work was motivated by the quest for a better porphycene sensitizer that generates singlet oxygen in high yield. In this study, we incorporated a heavy atom, bromine, directly substituted into the porphycene macrocycle as shown in Fig. 1, and that can promote intersystem crossing by way of spin–orbit coupling.[8] As a consequence, the singlet oxygen production ability *via* energy transfer from the triplet state of the porphycene will be enhanced. Furthermore, bromine substituents afford many advantages for photochemical reactions, not only to enhance the rate of intersystem crossing but also robust enough to prevent oxidation of the sensitizer itself, and causing a bathochromic shift of its absorption due to its electron withdrawing nature.

Brominated porphycenes (**2**, **3**, **4**, **5**) were synthesized by the reactions between bromine and **1**.[9] The number of bromine substituents was controlled by the amount of added bromine (ESI† Table S1). All of the brominated porphycenes were characterized by NMR, HRMS, and elemental analyses as well as X-ray analysis. Their crystal structures are shown in Fig. 2.[10]‡

The positions of bromine on each pyrrole ring of the porphycenes were clearly confirmed. The absorption, fluorescence and phosphorescence spectral data are summarized in Table 1. The Q-type absorption bands are red-shifted with increasing number of bromine groups of the porphycene (Fig. 3) while the fluorescence intensities decreased with increasing number of bromine groups (ESI† Fig. S1). Therefore, the rate of intersystem crossing would be expected to become greater.

Thus, we next measured the lifetimes of the singlet state (τ_S) for the porphycenes, and the results are also summarized in Table 1. The lifetimes decreased with increasing number of bromine groups. This result indicates the enhanced yield for the intersystem crossing to the triplet state. As a consequence, the yields of the singlet oxygen generation are expected to become greater. The quantum yields of the singlet oxygen generation (Φ_Δ) by a series of porphycenes were determined by the phosphorescence at 1270 nm in air-saturated solutions. The values increased with increasing number of bromine substituents, and the highest value of 0.95 was obtained for the dibrominated porphycene (**3**) as shown in Fig. 4. The values then decreased to 0.71 and 0.49 for the tri- (**4**) and tetra- (**5**) brominated porphycenes, respectively. To elucidate this bromine substitution effect, we obtained all the photophysical parameters and the results are summarized in Table 2.[11]

The fluorescence rate constants (k_f) are readily calculated using the measured values (Φ_f and τ_S) and eqn (1).

$$k_f = \Phi_f/\tau_S \quad (1)$$

The internal conversion rate constants (k_{ic}) and intersystem crossing rate constants (k_{isc}) are expressed by eqn (2) and (3).

$$k_{ic} = \Phi_{ic}/\tau_S \quad (2)$$

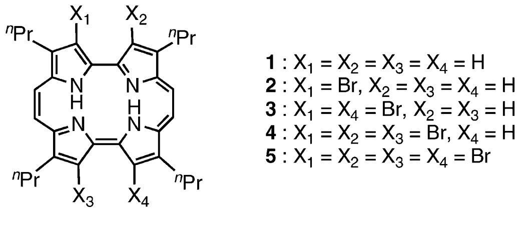

Fig. 1 Molecular structures of a series of porphycenes.

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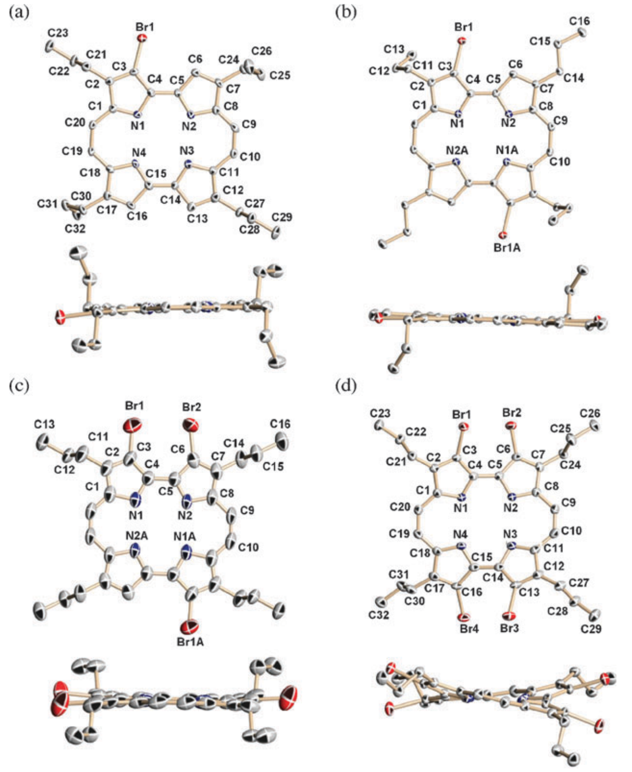

Fig. 2 Crystal structures of a series of brominated porphycenes (top and side views); (a) **2** (b) **3** (c) **4** (d) **5**, showing 50% displacement ellipsoids (H atoms are omitted for clarity). Atoms labelled with the suffix A are at symmetry related positions.

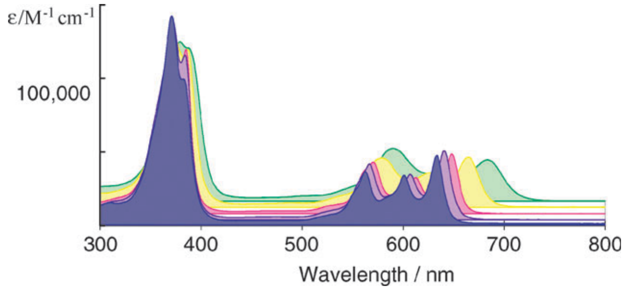

Fig. 3 UV-Vis spectra of a series of brominated porphycenes; (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** from front to back.

$$k_{isc} = \Phi_T/\tau_S \qquad (3)$$

The triplet quantum yield (Φ_T) and the internal conversion quantum yield (Φ_{ic}) are obtained as follows. As Φ_Δ can be expressed using eqn (4),[12]

$$\Phi_\Delta = \Phi_T P^T_{O2} f^T_\Delta \qquad (4)$$

Φ_T can be expressed by eqn (5),

$$\Phi_T = \Phi_\Delta / P^T_{O2} f^T_\Delta \qquad (5)$$

where P^T_{O2} is the proportion of the triplet quenched by $^3O_2$, and f^T_Δ is the fraction of the triplet quenched by $^3O_2$ leading to the formation of $^1O_2$. As P^T_{O2} can be expressed by eqn (6),

$$P^T_{O2} = k_q[O_2]/(k_p + k_{nr} + k_q[O_2]) \qquad (6)$$

($k_p + k_{nr}$) and k_q were determined from the Stern–Volmer analysis (ESI† Fig. S3) using eqn (7).

$$1/\tau_T = k_p + k_{nr} + k_q[O_2] \qquad (7)$$

where k_p is the phosphorescence rate constant, and k_{nr} is the rate constant of nonradiative decay. By using these parameters, P^T_{O2} was then calculated by eqn (6). The f^T_Δ value of **1** was determined to be 1.[13] In the case of **2–5**, the f^T_Δ were also estimated as 1 since the free energy change of the charge-transfer process ΔG_{CT} {$= F(E_{ox}{}^M - E_{red}{}^{O2}) - E_T$} where F is the Faraday constant, $E_{ox}{}^M$ is the half-wave oxidation potential of the sensitizer in the ground state, and $E_{red}{}^{O2}$ is the half-wave reduction potential of oxygen} of **2–5** are higher than that of **1**, so that the charge transfer process is suppressed by bromination to induce the enhancement of the sensitization efficiency f^T_Δ. Thus Φ_T can be calculated from eqn (4). Finally, the singlet state (S_1) may decay *via* a radiative process, which produces a fluorescence emission, or through non-radiative processes, including internal conversion (ic) to the ground state (S_0) or intersystem crossing (isc) to the excited triplet state (T_1), Φ_{ic} can be expressed by eqn (8).

$$\Phi_{ic} = 1 - (\Phi_T + \Phi_f) \qquad (8)$$

The calculated parameters, ($k_p + k_{nr}$), k_q, P^T_{O2} and ΔG_{CT} for **1–5** are summarized in Table S2 of ESI.†

As expected, the rate of intersystem crossing (k_{isc}) increased with the increasing number of bromines even for the tri- (**4**) and tetra- (**5**) brominated porphycene. Remarkably, the rate of internal conversion (k_{ic}) is significantly increased between the di- (**3**) and tri- (**4**) brominated porphycenes. The effects of the bromine groups are shown in Fig. 5.

For **4** and **5**, the increase in the k_{ic} value reduced their ratio of intersystem crossing, so that the quantum yield of the singlet oxygen generation decreased. Steric hindrance between two neighboring bromine groups in **4** and **5** distort the porphycene macrocycle.[14] The flexibility caused by this distortion should then enhance the internal conversion rate.[15]

Table 1 Photophysical data of a series of porphycenes[a]

Compound	$\lambda_{abs}{}^b$/nm ($10^{-3}\varepsilon$/M^{-1} cm^{-1})	$\lambda_{fluo}{}^c$/nm	$\lambda_{phos}{}^{de}$/nm	$\tau_S{}^{ef}$/ps	$\tau_T{}^{ceg}$/μs
1	371 (142), 562 (35.3), 601 (33.3), 633 (46.4)	644, 702	978	8920	85
2	371 (125), 383 (102), 567 (34.7), 607 (28.4), 641 (43.8)	648, 712	990	1400	39
3	372 (132), 385 (133), 571 (40.7), 613 (29.0), 649 (47.3)	658, 719	996	754	23
4	375 (113), 387 (108), 579 (34.0), 625 (23.8), 665 (34.6)	659, 683	1053	103	8
5	379 (107), 590 (36.0), 640 (20.6), 684 (29.0)	649, 716	—[h]	53	2

[a] λ_{abs}: absorption maximum; λ_{fluo}: fluorescence maximum; λ_{phos}: phosphorescence maximum; τ_S and τ_T: lifetimes of the singlet and triplet states. [b] Solvent, CH_2Cl_2. [c] Solvent, toluene. [d] Solvent, bromobenzene. [e] Degassed under vacuum. [f] Degassed under nitrogen. [g] Excitation at 532 nm. [h] Low intensity peak around 1100–1200 nm.

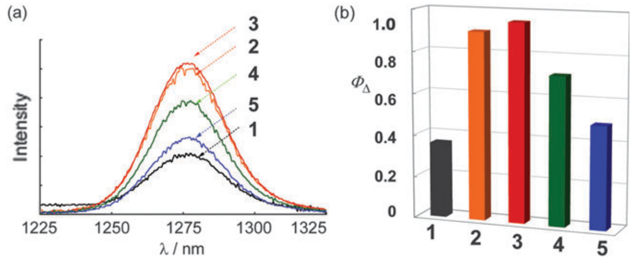

Fig. 4 (a) Phosphorescence spectra of singlet oxygen sensitized by a series of porphycenes in air-saturated toluene at r.t. with excitation at 600 nm. (b) Comparison of Φ_Δ values for a series of porphycenes.

Table 2 Photophysical parameters of a series of porphycenes[ab]

Compound	Φ_f[c]	Φ_{ic}	Φ_T	Φ_Δ	10^{-7} k_f/s^{-1}	10^{-7} k_{ic}/s^{-1}	10^{-7} k_{isc}/s^{-1}
1	0.37	0.27	0.36	0.36	4.1	3.0	4.0
2	0.08	0.02	0.90	0.90	5.7	1.4	64
3	0.03	0.02	0.95	0.95	4.0	2.7	130
4	0.006	0.27	0.72	0.71	5.8	260	700
5	0.002	0.46	0.53	0.49	3.8	870	1000

[a] Φ_f: Fluorescence quantum yield; Φ_{ic}: internal conversion quantum yield; Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen production quantum yield. [b] Solvent, toluene. [c] Determined by absolute and relative methods for **1–3** and **4–5**, respectively. Degassed under nitrogen.

Finally, catalysis of the porphycene for photo-oxygenation of 1,5-dihydroxynaphthalene was investigated ([sensitizer] = 1.28 μM, [substrate] = 3.33 mM, solv. CH_2Cl_2–MeOH (9 : 1 v/v) in air at r.t. with a 500 W tungsten lamp ($\lambda \geq 460$ nm)). As expected, the photoreaction effectively proceeded and the oxygenated product, 5-hydroxy-1,4-naphthoquinone, was quantitatively obtained within 1 h in the case of **3**. In contrast, tetraphenylporphyrin (H_2TPP) and tetrakis(2,6-dichlorophenylporphyrin (H_2TPPCl_8) yield only 12 and 29% of the product, respectively, regardless of their high Φ_Δ values (0.88 for H_2TPP, 0.98 for H_2TPPCl_8).[7,8] The advantage of the porphycene over porphyrin in the photoreaction is due to its more effective light absorption in the visible region. Furthermore, the porphycene did not show bleaching during irradiation by visible light (ESI†).

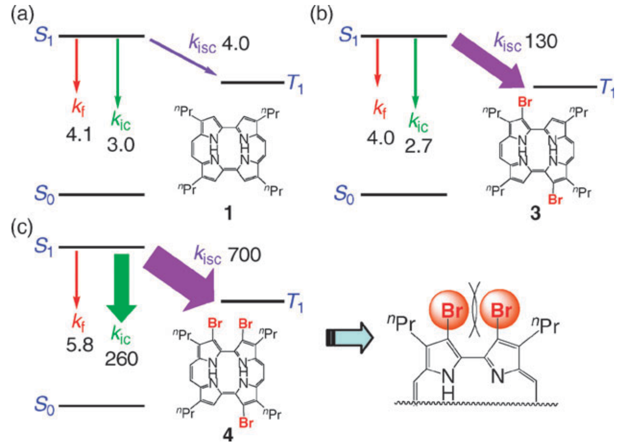

Fig. 5 Schematic representations of effects of bromine groups. The rate constants (k_f, $k_{ic}$and $k_{isc}/10^7$ s^{-1}) are from Table 2.

In conclusion, the photophysical properties of a series of brominated porphycenes were clarified such that their photophysical parameters are dependent on the number of bromines. Especially, the dibrominated porphycene shows the highest sensitization efficiency for singlet oxygen production in response to visible light.

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Notes and references

‡ Crystallographic data are given in the ESI.† Compounds **3** and **4** have crystallographically imposed inversion symmetry.

1. J. L. Sessler, A. Gebauer and E. Vogel, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R Guilard, Academic Press, New York, 2000, ch. 8, vol. 2, pp. 1–54.
2. E. Vogel, M. Köcher, H. Schmickler and J. Lex, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 257–259.
3. (*a*) J. Waluk, M. Müller, P. Swiderek, M. Köcher, E. Vogel, G. Hohlneicher and J. Michl, *J. Am. Chem. Soc.*, 1991, **113**, 5511–5527; (*b*) T. Hayashi, H. Dejima, T. Matsuo, H. Sato, D. Murata and Y. Hisaeda, *J. Am. Chem. Soc.*, 2002, **124**, 11226–11227; (*c*) J. Hasegawa, K. Takata, T. Miyahara, S. Neya, M. J. Frisch and H. Nakatsuji, *J. Phys. Chem. A*, 2005, **109**, 3187–3200; (*d*) D. Sánchez-Ganchez and J. L. Sessler, *Chem. Soc. Rev.*, 2008, **37**, 215–232.
4. (*a*) S. E. Braslavsky, M. Müller, D. O. Mártire, S. Pörting, S. G. Bertolotti, S. Chakravorti, G. Koc-Weier, B. Knipp and K. Schaffer, *J. Photochem. Photobiol., B*, 1997, **40**, 191–198; (*b*) J. C. Sockert, M. Canete, A. Juarranz, A. Villanueva, R. W. Horobin, J. K. Borrell, J. Teixido and S. Nonell, *Curr. Med. Chem.*, 2007, **14**, 997–1026; (*c*) T. Baba, H. Shimakoshi, A. Endo, C. Adachi and Y. Hisaeda, *Chem. Lett.*, 2008, **3**, 264–265.
5. (*a*) R. Bonnett, *Chem. Soc. Rev.*, 1995, 19–33; (*b*) R. K. Pandey and G. Zheng, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R Guilard, Academic Press, New York, 2000, ch. 43, vol. 6, pp. 157–230; (*c*) A. Greer, *Acc. Chem. Res.*, 2006, **39**, 797–804.
6. P. F. Aramendia, R. W. Redmond, N. Santiago, W. Schuster, S. E. Braslavsky, K. Schaffner and E. Vogel, *Photochem. Photobiol.*, 1986, **44**, 555–559.
7. (*a*) R. W. Redmond and J. N. Gamlin, *Photochem. Photobiol.*, 1999, **70**, 391–475; (*b*) T. Nyokong, *Coord. Chem. Rev.*, 2007, **251**, 1707–1722.
8. E. G. Azenha, A. C. Serra, M. Pineiro, M. M. Pereira, J. S. Melo, L. G. Arnaut, S. J. Formosinho and A. M. d'A. R. Gonsalves, *Chem. Phys.*, 2002, **280**, 177–190.
9. (*a*) S. Will, A. Rahbar, H. Schmickler, J. Lex and E. Vogel, *E. Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1390–1393; (*b*) I. Aritome, H. Shimakoshi and Y. Hisaeda, *Acta Crystallogr., Sect. C*, 2002, **58**, o563–o564; (*c*) T. Baba, H. Shimakoshi, I. Aritome and Y. Hisaeda, *Chem. Lett.*, 2004, **33**, 906–907. In these papers, the authors described the syntheses of the mono- (**2**), tri- (**4**) and tetra- (**5**) brominated porphycenes.
10. Tetra-brominated porphycene **5** affords three kinds of crystal structures. Form III is described in this paper for the first time.
11. The photophysical data for **1** have also been reported: N. Rubio, F. Prat, N. Bou, J. I. Borrell, J. Teixido, A. Villanueva, A. Juarranz, M. Canete, J. C. Stockert and S. Nonell, *New J. Chem.*, 2005, **29**, 378–384.
12. D. García-Fresnadillo, Y. Georgiadou, G. Orellana, A. M. Braun and E. Oliveros, *Helv. Chim. Acta*, 1996, **79**, 1222–1238.
13. S. Nonell, P. F. Aramendía, K. Heihoff, R. M. Negri and S. E. Braslavsky, *J. Phys. Chem.*, 1990, **94**, 5879–5883.
14. The distortion of **4** is reduced in the crystal as shown in Fig. 2 by π–π stacking between the aromatic rings: see crystallographic data in CCDC 677020.
15. I. V. Sazannovich, V. A. Galievsky, A. v. Hoek, T. J. Schaafsma, V. L. Malinovskii, D. Holten and V. S. Chirvony, *J. Phys. Chem. B*, 2001, **105**, 7818–7829.