

A novel parachute-shaped C₆₀-porphyrin dyad

Peng Cheng, Stephen R. Wilson and David I. Schuster*

Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, USA.
E-mail: david.schuster@nyu.edu

Received (in Corvallis, OR, USA) 14th September 1998, Accepted 23rd November 1998

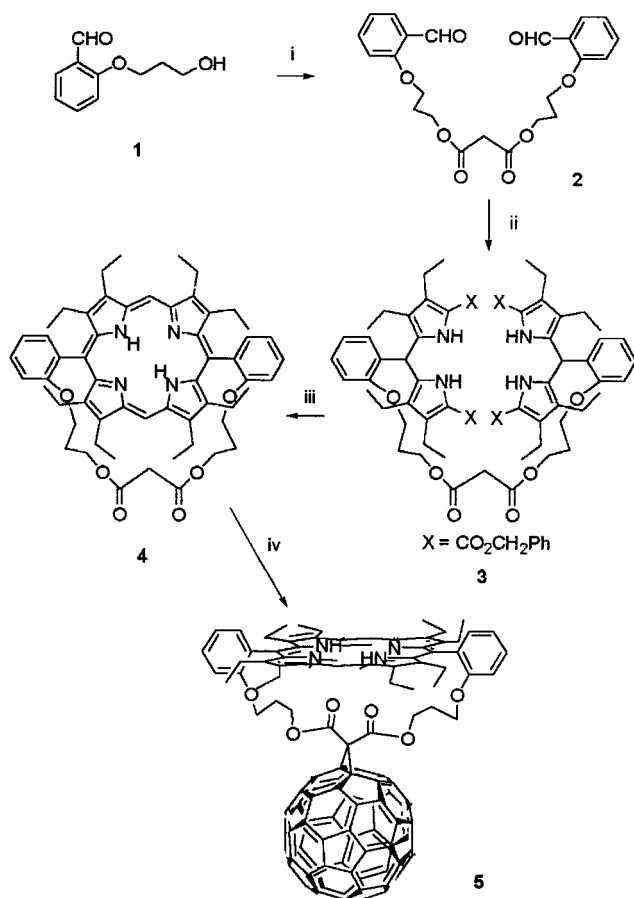
A novel covalently linked C₆₀-porphyrin dyad has been prepared by cyclopropanation of C₆₀ with a strapped porphyrin malonate; its fluorescence spectrum shows strong quenching of the porphyrin singlet excited state by the attached C₆₀.

Photosynthetic model systems rely on spatially organized units with suitable photochemical and electronic properties. Recently much attention has been focused on using C₆₀ as the electron acceptor in donor-acceptor systems due to its unique shape and redox properties.¹⁻³ To continue a project aimed at studying interactions between two chromophores in covalently linked C₆₀-porphyrin dyads with flexible and rigid tethers,³ we became interested in the synthesis of a novel parachute-shaped dyad in which the two π -systems are forced into a face-to-face arrangement.

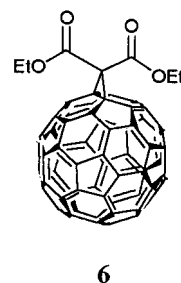
We synthesized a key intermediate porphyrin **4** using a strapped porphyrin strategy⁴ in order to avoid tedious chromatographic separation of two *ortho*-linked atropisomers (Scheme 1). Esterification of 2-(3-hydroxypropyl)benzaldehyde with

malonyl dichloride gave compound **2**. Condensation of the dialdehyde with 4 equiv. of benzyl 3,4-diethylpyrrole-2-carboxylate⁵ gave compound **3**. Hydrogenation of **3** followed by reaction with methyl orthoformate catalyzed by trichloroacetic acid led to strapped porphyrin **4**, which was separated in 12% yield by flash column chromatography (silica gel, CH₂Cl₂-MeOH 20:1). The porphyrin malonate was then attached to C₆₀ via Bingel cyclopropanation⁶ accomplished by the action of CBr₄ and DBU.⁷ The dyad **5**[†] was isolated in 25% yield by preparative TLC (silica gel, CH₂Cl₂-MeOH 25:1).

The structure of dyad **5** was confirmed by spectral data including ¹H MMR, ¹³C NMR, ³He NMR, UV-VIS and MALDI-TOF mass spectra.[‡] The ¹H NMR spectrum in CDCl₃ exhibits the expected features with correct integration ratios, which is similar to the spectrum of porphyrin **4** except for the disappearance of the two protons on the methylene carbon between the two carbonyl groups. The ¹³C NMR spectrum of **5** shows eight of the nine resonances for the sp³ carbon atoms, 24 of the 28 resonances in the region δ 97.0–160.0 arising from the sp² carbon atoms of the C₆₀ moiety and the porphyrin, as well as a resonance (δ 161.53) for the malonate carbonyl groups, clearly demonstrating that dyad **5** has C_{2v} symmetry. Interestingly, the dyad made from ³He@C₆₀ shows a peak at δ -8.5 relative to ³He gas via ³He NMR spectroscopy, whereas typical methano-1,2-dihydrofullerenes-C₆₀ like **6** have a ³He NMR



Scheme 1 Reagents and conditions: i, malonyl dichloride, Et₃N, CH₂Cl₂, 0 °C; ii, benzyl 3,4-diethylpyrrole-2-carboxylate, HCl, EtOH, reflux, 5 h; iii, H₂, 10% Pd/C, Et₃N, THF, room temp., 5 h, then CH(OCH₃)₃, Cl₃CCO₂H, CH₂Cl₂, room temp., 48 h; iv, C₆₀, CBr₄, DBU, toluene, room temp.



resonance at δ -8.1.⁸ The upfield shift is attributable to the shielding effect of the porphyrin ring current. Calculations indicate that the average distance between the center of the four pyrrole N atoms and the center of the two sp³ carbons on the C₆₀ is 6.4 Å in the CVFF minimized structure (InsightII 97.2, Discover 3). The two tethers make the system relatively rigid.

The UV-VIS spectrum of **5** displays strong absorption bands due to both the porphyrin and fullerene moieties. Fig. 1 shows the UV-VIS spectrum of **5** together with that of porphyrin **4** and **6** for comparison. Since the porphyrin dominates the visible region whereas C₆₀ dominates the UV region, the electronic spectrum of **5** is a virtual superimposition of the two independent chromophores present in the molecule, indicating no appreciable ground state interaction between the two π -systems.

In CH₂Cl₂, porphyrin **4** displays fluorescence maxima at 635 and 698 nm (Fig. 2). The dyad **5**, excited at 580 nm, shows an emission spectrum with characteristic features of the porphyrin. However, the porphyrin emission is efficiently quenched by the attached C₆₀ by a factor of 40. It remains to be clarified from time-dependent measurements whether the quenching of the

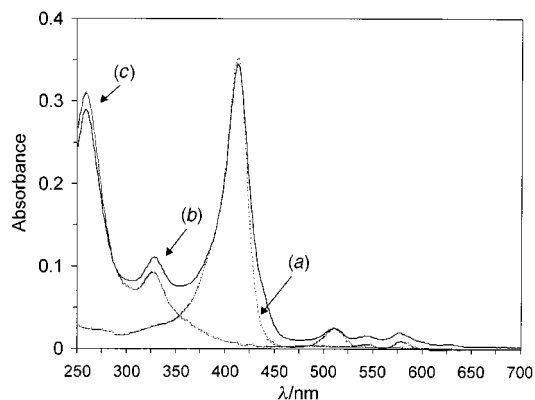


Fig. 1 UV-VIS spectra of (a) **4**, (b) **5** and (c) **6** in CH_2Cl_2 (2.5×10^{-6} mol dm^{-3}).

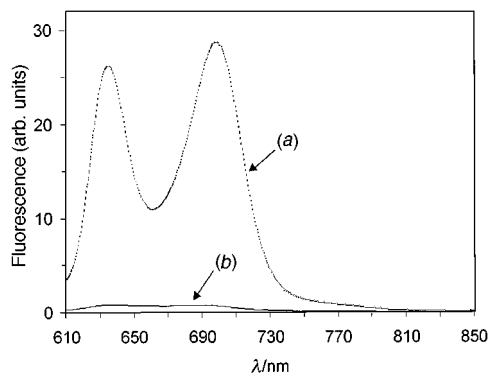


Fig. 2 Fluorescence spectra of (a) **4** and (b) **5** in CH_2Cl_2 (2.5×10^{-6} mol dm^{-3}).

porphyrin fluorescence results from photoinduced energy transfer and/or electron transfer.

We thank Dr Anthony Khong (Yale University) for the ^3He NMR measurement. Financial support of this research by the US National Science Foundation is gratefully acknowledged. We also thank Andreas Hirsch (Erlangen) and François Diederich (ETH, Zürich) for communication prior to publication of independent synthesis of rigid C_{60} -porphyrin cyclophanes.²

Notes and references

† Detailed procedures for the synthesis and spectroscopic data of **4** and **5** will be reported elsewhere.

‡ Selected data for **5**: δ_{H} (200 MHz, CDCl_3 , 25 °C) 10.33 (2H, s), 8.57 (2H, d), 7.80 (2H, t), 7.46 (2H, t), 7.13 (2H, d), 4.09 (8H, q), 3.80 (4H, t), 3.18 (4H, m), 2.72 (4H, m), 2.16 (4H, t), 1.97 (12H, t), 1.22 (12H, t), 1.11 (4H, m), -1.90 (2H, br s); δ_{C} (75 MHz, CDCl_3 , 25 °C) 161.53, 159.83, 145.44, 145.06, 144.98, 144.90, 144.53, 144.39, 144.29, 143.58, 142.85, 142.75, 142.67, 141.95, 141.61, 141.09, 140.62, 138.06, 134.03, 131.75, 130.45, 120.21, 113.46, 112.83, 97.27, 65.01, 63.37, 32.35, 27.89, 20.78, 19.91, 18.47, 17.48; δ_{He} (500 MHz, 1-methylnaphthalene- CD_2Cl_2) -6.5 ($^3\text{He}@C_{60}$), -8.5 ($^3\text{He}@5$); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 259 (115600), 328 (44400), 412 (138000), 510 (10000), 544 (6400), 577 (7600); fluorescence ($\lambda_{\text{exc}} = 580 \text{ nm}$) $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 698, 635; m/z (MALDI-TOF) 1622.3 (M + H⁺), calc. 1622.8 (M + H⁺).

- For examples, see P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore and D. Gust, *Photochem. Photobiol.*, 1994, **60**, 537; H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada and Y. Sakata, *Chem. Lett.*, 1995, 265; T. Drovetskaya, C. A. Reed and P. Boyd, *Tetrahedron Lett.*, 1995, **36**, 7971; M. G. Ranasinghe, A. M. Oliver, D. F. Rothenfluh, A. Salek and M. N. Paddon-Row, *Tetrahedron Lett.*, 1996, **37**, 4797; H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada and Y. Sakata, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2626; D. Carbonera, M. Di Valentin, C. Corvaja, G. Agostini, G. Giacometti, P. A. Liddell, D. Kuciauskas, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 1998, **120**, 4398; E. Dietel, A. Hirsch, J. Zhou and A. Rieker, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1357.
- E. Dietel, A. Hirsch, E. Eichhorn, A. Rieker, S. Hackbarth and B. Roder, *Chem. Commun.*, 1998, 1981; J.-P. Bourgeois, F. Diederich, L. Echegoyen and J.-F. Nierengarten, *Helv. Chim. Acta*, 1998, **81**, 1835.
- P. S. Baran, R. R. Monaco, A. U. Khan, S. R. Wilson and D. I. Schuster, *J. Am. Chem. Soc.*, 1997, **119**, 8363; I. G. Safanov, P. S. Baran and D. I. Schuster, *Tetrahedron Lett.*, 1997, **38**, 8133; R. Fong II, D. I. Schuster, H. Mi, S. R. Wilson and A. U. Khan, *Proc. Electrochem. Soc.*, 1998, **98**, 262.
- J. E. Baldwin, M. J. Crossley, T. Klose, E. A. O'Rear III and M. K. Peters, *Tetrahedron*, 1982, **38**, 27.
- T. D. Lash, J. R. Bellettini, J. A. Bastian and K. B. Couch, *Synthesis*, 1994, 170.
- C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
- X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1595.
- R. J. Cross, H. A. Jiménez-Vázquez, Q. Lu, M. Saunders, D. I. Schuster, S. R. Wilson and H. Zhao, *J. Am. Chem. Soc.*, 1996, **118**, 11454.

Communication 8/07214K