A novel parachute-shaped C₆₀-porphyrin dyad

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A novel covalently linked C_{60} -porphyrin dyad has been prepared by cyclopropanation of C_{60} with a strapped porphyrin malonate; its fluorescence spectrum shows strong quenching of the porphyrin singlet excited state by the attached C_{60} .

Photosynthetic model systems rely on spatially organized units with suitable photochemical and electronic properties. Recently much attention has been focused on using C_{60} 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 C_{60} –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



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.

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



resonance at $\delta - 8.1.^8$ 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 C_{60} 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 C_{60} 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.

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Notes and references

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

[‡] Selected data for **5**: δ_H(200 MHz, CDCl₃, 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, CDCl₃, 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-CD₂Cl₂) -6.5 (³He@C₆₀), -8.5 (³He@ **5**); λ_{max}(CH₂Cl₂)/m (ε/dm³ mol⁻¹ cm⁻¹) 259 (115600), 328 (44400), 412 (138000), 510 (10000), 544 (6400), 577 (7600); fluorescence (λ_{exc} = 580 nm) λ_{max}(CH₂Cl₂)/m 698, 635; *m/z* (MALDI-TOF) 1622.3 (M + H⁺), calc. 1622.8 (M + H⁺).

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