Pergamon

Tetrahedron Letters 43 (2002) 4919–4922

TETRAHEDRON
LETTERS

Photoinduced electron transfer within porphyrin–cyclodextrin conjugates

Kamil Lang,[a,*] Vladimír Král,[b] Petr Kapusta,[c] Pavel Kubát[d] and Petr Vašek[b]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic*
[b] *Institute of Chemical Technology, Technická 5, 166 28 Praha 6, Czech Republic*
[c] *Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, V Holešovičkách 2, 180 00 Praha 8, Czech Republic*
[d] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic*

Received 15 April 2002; revised 3 May 2002; accepted 17 May 2002

Abstract—Reaction of β-cyclodextrin alcoholate with *meso*-tetrakis(pentafluorophenyl)porphyrin under mild conditions afforded a hydrophilic cyclodextrin–porphyrin conjugate in 14% yield. The conjugate showed a marked tendency to form chiral assemblies in aqueous solutions. Photoinduced electron transfer, occurring within the conjugate monomer or aggregate, between the porphyrin moiety and a guest molecule accommodated in the cyclodextrin cavity was investigated by fluorescence spectroscopy.

Porphyrin assemblies[1] and high-order structures[2,3] are attractive due to their structural resemblance to the chlorophyll aggregates and other molecular systems relevant to biology. Although photophysical and photochemical properties of monomer porphyrins in solutions are well characterized, less is known about the effects of strong electronic interactions between coupled porphyrin rings on intramolecular photoinduced processes.[4,5] Photoinduced electron transfer processes have been studied on many elegant covalent systems, but more biologically relevant non-covalent donor/acceptor assemblies, based on salt bridges, hydrogen bonding or inclusion, have been addressed recently.[6] Construction of porphyrin–cyclodextrin conjugates affords molecules that combine useful photoactive and/or electroactive properties of the porphyrin moiety and the binding ability of the hydrophobic pre-organized cyclodextrin (CD) cavity. Cyclodextrins are water-soluble cyclic oligosaccharides forming inclusion complexes with a number of compounds such as water-soluble porphyrins.[7] The synthesis and characterization of several CD-linked porphyrins have been reported.[8–14] They were used for studying binding and catalytic,[8–10] photocatalytic[11] and photoinduced electron transfer[12] processes. Here we report on a novel modular approach for the synthesis of porphyrin–CD conjugates joined by the -O-CH_2 bridges and on spectral properties of porphyrin assemblies bearing the CD cavity. Several compounds were specifically incorporated into the CD cavity and photoinduced electron transfer that includes the compound and neighboring porphyrin units was investigated by fluorescence spectroscopy.

The synthesis relies on the use of *meso*-tetrakis(pentafluorophenyl)porphyrin **1** and β-CD alcoholate. Mixing equimolar amounts of **1** and β-CD alcoholate[15] (formed from dispersed β-CD by treatment with NaH in dry dioxane) in dry DMF resulted in the formation of conjugates. A conjugate bearing one CD **2** (Fig. 1) was obtained under mild conditions at room temperature, while treatment at 90°C for 6 h afforded a conjugate with four CDs *per* porphyrin unit attached at each 4-fluorophenyl substituent. Reaction products were purified by reverse-phase chromatography and fully identified by ^1H, ^{19}F, ^{13}C NMR, MALDI TOF-MS spectroscopy and elemental analysis.[16]

Porphyrin **1** is a hydrophobic porphyrin soluble in methanol. The attachment of β-CD having a hydrophilic exterior produces a conjugate soluble in aqueous solutions. The absorption spectrum of a methanolic solution of **2** is characterized by the intense

---

Keywords: porphyrin–cyclodextrin; chiral aggregate; quenching; electron transfer.

* Corresponding author. Tel.: +420-2-6617 2193; fax: +420-2-2094 1502; e-mail: lang@iic.cas.cz

PII: S0040-4039(02)00954-1

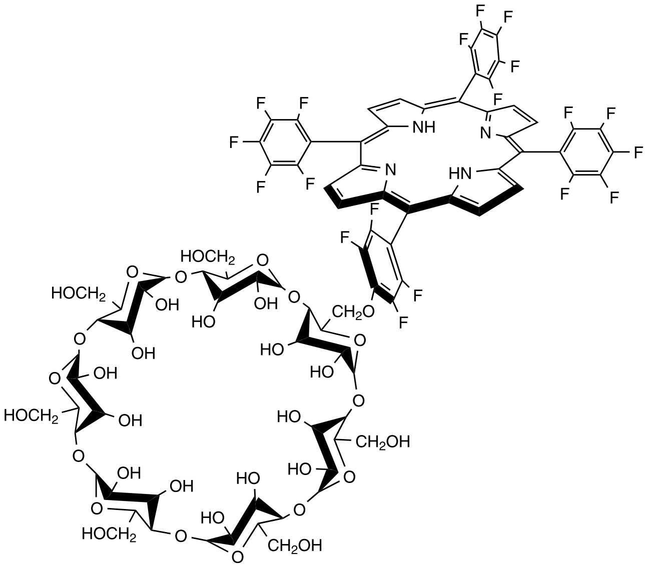

Figure 1. Porphyrin–CD conjugate **2**.

Soret band at 408 nm (2.3×10^5 M^{-1} cm^{-1}) and by the Q-bands at 504, 535, 581 and 635 nm (Fig. 2a). This spectrum is fully comparable with that of **1** with typical low intensities at 535 and 635 nm due to the electron-withdrawing character of the pentafluorophenyl substituents.[17] Similarly, the fluorescence emission peaks of **2** at 643 and 709 nm and the fluorescence quantum yield Φ_f of 0.061 (methanol) are the same as those of **1**.[17] This demonstrates that the attachment of CD does not affect the spectral properties of the porphyrin moiety of **2**. In aqueous solutions, the Soret band of **2** is considerably broadened and shows a large hypochromicity ($\varepsilon_{412}=1.1\times10^5$ M^{-1} cm^{-1}) (Fig. 2b). These changes are accompanied by a shift of the emission bands to 666 nm and 713 nm and by a strong decrease of Φ_f from 0.061 (methanol) to 0.029. Similarly, the quantum yields of the triplet states Φ_T are quenched from 0.63 in methanol to ~0.01 in a buffer solution. In order to obtain more information on the molecular form of **2** we performed resonance light scattering experiments (RLS). Because the amount of scattered light is directly proportional to the volume of particles and because monomeric molecules and small oligomers show no enhanced scattering it makes this method particularly useful.[18,19] In a phosphate buffer, we recorded intense RLS profiles confirming the formation of extended assemblies of **2**. The peaks centered at about 436 nm are slightly red-shifted compared to the Soret band of **2** in consequence of self-absorption of scattered light near the Soret maxima (Fig. 2d). Intermolecular contacts within the assembly[13,20,21] are also documented by the strong induced circular dichroism at 420 nm (Fig. 3). In methanol, monomeric **2** shows only the minimum at the Soret band of RLS due to self-absorption of the incident light (Fig. 2c) and no circular dichroism in the Soret region. All described spectral features point to exciton coupling between adjacent porphyrin units due to the formation of chiral assemblies of **2** in aqueous solutions.

The key role of CD in the formation of a porphyrin-based supramolecular complex is confirmed by steady-state and time-resolved fluorescence data summarized in Table 1. The fluorescence intensity of **2** is quenched by the addition of 1,4-benzoquinone (BQ), anthraquinone-2-sulfonate (AQS) and 8-anilino-1-naphthalene sulfonic acid (ANS) in 20 mM phosphate buffer. All these quenchers are known to form inclusion complexes with β-CDs in aqueous media.[22] Since **2** has one CD binding site we can assume a 1:1 complex formation. Quenching is characterized by the downward curving of the Stern–Volmer plots indicating a complex process. The fluorescence lifetime of **2** in methanol (10.6 ns) is similar to that of **1** (9.6 ns) and can be attributed to the sole presence of the porphyrin monomer. In a buffer solution of pH 7.1, the fluorescence decay of **2** becomes biexponential with lifetimes of 4.6 and 10.9 ns. The longer lifetime belongs to the porphyrin monomer and the lifetime of 4.6 ns can be tentatively attributed to the porphyrin assembly because the fluorescence lifetimes tend to decrease upon porphyrin aggregation.[4,5] As follows from Table 1 both lifetimes decrease upon addition of AQS or ANS. The longer-living monomer is quenched by AQS more effectively than the assembled form as documented by a decrease of the relative amplitude from 69 to 49%. This observation can explain the observed non-linearity of the Stern–Volmer plots. We also monitored the fluorescence changes of **2** caused by the quenchers in the presence of 1-adamantanecarboxylic acid (Ad), which is known to be incorporated into the CD cavity with large affinity and thus it displaces the quencher molecule.[22]

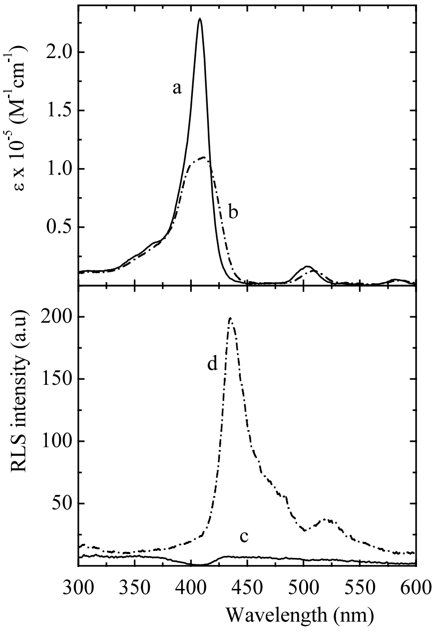

Figure 2. Absorption spectra of **2** in methanol (a) and in 20 mM phosphate buffer, pH 7.1 (b). Resonance light-scattering profiles of **2** in methanol (c) and in 20 mM phosphate buffer, pH 7.1 (d).

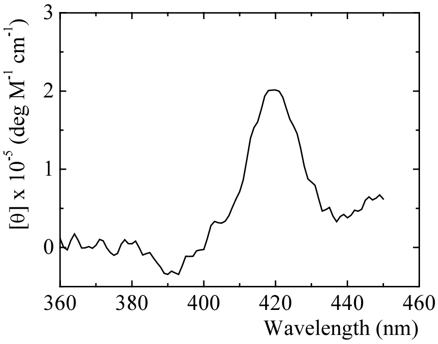

Figure 3. Circular dichroism spectrum of **2** (3 μM) in water at room temperature.

Table 1. Summary of fluorescence lifetimes[a] of **2** in 20 mM phosphate buffer, pH 7.1. The numbers in parentheses indicate the relative amplitudes of the components

Quencher	τ_1 (ns)	τ_2 (ns)
–[b]	–	10.6 (100%)
–[c]	4.6 (31%)	10.9 (69%)
4.4 mM Ad	4.9 (28%)	11.2 (72%)
0.31 mM AQS	4.2 (40%)	9.3 (60%)
0.77 mM AQS	3.8 (45%)	8.6 (55%)
2.3 mM AQS	3.3 (51%)	8.0 (49%)
0.77 mM AQS, 3.7 mM Ad	4.2 (35%)	9.4 (65%)
0.1 mM ANS	1.7 (75%)	4.4 (25%)
0.1 mM ANS, 3.6 mM Ad	2.5 (71%)	7.1 (29%)

[a] Fluorescence decay kinetics was measured on an Edinburgh Instruments FS/FL900 steady-state/time-resolved spectrofluorimeter using time-correlated single photon counting detection. The samples in 1 cm quartz cells were excited at 403.7 nm and fluorescence was collected at 720 nm. Fluorescence lifetimes were determined by non-linear least-squares iterative re-convolution fitting of the raw data. The quality of the fit was evaluated by inspection of the residual distribution and the reduced χ^2 value.

[b] Solution in methanol; recorded at 709 nm; fluorescence quantum yield $\Phi_f = 0.061$; quantum yield of the triplet states $\Phi_T = 0.63$, lifetime of the triplet states $\tau_T = 2.8$ ms. The triplet states were recorded using a laser kinetic spectrometer (Applied Photophysics).

[c] $\Phi_f = 0.029$, $\Phi_T \approx 0.01$.

While Ad has no significant effect on fluorescence of **2** itself, in the presence of the quenchers Ad increases the fluorescence intensity, the lifetimes and the contribution of the longer-living fluorescent component (Table 1). The results presented and the fact that fluorescence quenching of **2** does not occur in methanol in which the quenchers are not bound, confirm that intermolecular porphyrin–quencher interactions are not responsible for the observed fluorescence quenching, and that fluorescence quenching occurs via an intramolecular process.

On the basis of the displacement by Ad, the oxidative and reductive electron transfer potential[23] of BQ, AQS and ANS, respectively, fluorescence quenching can be interpreted in terms of electron transfer between the excited porphyrin moiety and the quencher molecule accommodated in the CD cavity. Photoinduced electron transfer occurs in both monomeric and assembled forms of porphyrin **2**, which is directly demonstrated by the lowering of the lifetimes both in biexponential fluorescence kinetics.

In conclusion, the developed synthetic procedure offers versatile molecular conjugates of porphyrins bearing one or more CD units that are suitable for systematic investigation of photoinduced processes within noncovalently bound supramolecular systems. We have demonstrated that intramolecular electron transfer between the porphyrin moiety and the quencher accommodated in the CD cavity dominates over intermolecular electron transfer and/or the formation of the porphyrin triplet states.

Acknowledgements

The authors gratefully acknowledge the support of the Grant Agency of the Czech Republic (203/99/1163, 203/01/0634, 203/02/1483, 203/02/0933).

References

1. van Esch, J. H.; Feiters, M. C.; Peters, A. M.; Nolte, R. J. M. *J. Phys. Chem.* **1994**, *98*, 5541–5551.
2. Lammi, R. K.; Ambroise, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579–7591.
3. Anderson, H. L. *Chem. Commun.* **1999**, 2323–2330.
4. Akins, D. L.; Ozcelik, S.; Zhu, H.-R.; Guo, C. *J. Phys. Chem.* **1996**, *100*, 14390–14396.
5. Maiti, N. C.; Ravikanth, M.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem.* **1995**, *99*, 17192–17197.
6. Hayashi, T.; Ogoshi, H. *Chem. Soc. Rev.* **1997**, *26*, 355–364.
7. Mosinger, J.; Deumié, M.; Lang, K.; Kubát, P.; Wagnerová, D. M. *J. Photochem. Photobiol. A: Chem.* **2000**, *130*, 13–20.
8. Breslow, R.; Zhang, X.; Huang, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4535–4536.
9. Yang, J.; Breslow, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 2692–2694.
10. French, R. R.; Holzer, P.; Leuenberger, M. G.; Woggon, W.-D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1267–1269.
11. Weber, L.; Imiolczyk, I.; Haufe, G.; Rehored, D.; Hennig, H. *J. Chem. Soc., Chem. Commun.* **1992**, 301–303.
12. Kuroda, Y.; Ito, M.; Sera, T.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 7003–7004.
13. Carofiglio, T.; Fornasier, R.; Lucchini, V.; Simonato, L.; Tonellato, U. *J. Org. Chem.* **2000**, *65*, 9013–9021.
14. Chen, W.-H.; Yan, J.-M.; Tagashira, Y.; Yamaguchi, M.; Fujita, K. *Tetrahedron Lett.* **1999**, *40*, 891–894.
15. Procedure for the synthesis of β-CD alcoholate: β-CD (1000 mg; 0.88 mmol) was dispersed in dry dioxane (25 ml) and NaH (30 mg; 1.27 mmol) was added. The mixture was stirred under argon for 6 h. The solvent was removed under reduced pressure. The product was stored under an argon atmosphere and used as a starting compound, without further purification, for the synthesis of **2**.

16. Procedure for synthesis of **2**: β-CD alcoholate (240 mg; 0.21 mmol) and **1** (200 mg; 0.21 mmol) were mixed in an equimolar ratio in dry DMF (10 ml) and stirred at room temperature. The solvent was removed under reduced pressure. The solid residue was purified by reverse-phase chromatography (LiChroprep RP-18; Merck, 30 g), eluting with water–methanol gradient (3:7–1:9) to yield pure **2** (62 mg; 14% yield) as a purple microcrystalline powder. Chemical shifts of protons and carbons are relative to TMS, the fluorine shifts are relative to $CFCl_3$; all in ppm. Compound **2**: ^{1}H NMR (CD_3OD, 400 MHz), selected resonances δ: 7.98 (8H, s, β-pyrrolic H), 5.5–2.7 (β-CD H). ^{19}F NMR (CD_3OD, 282.2 MHz) δ: −138.5 (6F, m), −140.54 (2F, dd, $J_1=6.7$ Hz, $J_2=14.9$ Hz), −153.80 (3F, t, $J=20.1$ Hz), −156.42 (2F, dd, $J_1=7.7$ Hz, $J_2=14.6$ Hz), −163.37 (6F, m). ^{13}C NMR (DMSO-d_6) selected resonances δ: 103.91 (CD CH), 83.03 (CD CH), 74.83 (CD CH), 74.64 (CD CH), 74.27 (CD CH), 73.80 (CD CH), 61.95 (CD CH_2). UV–VIS (MeOH) λ_{max} (nm), ε (M^{-1} cm^{-1}) in parentheses: 408 (2.28×10^5), 504 (1.80×10^4), 535 (2.2×10^3), 581 (5.9×10^3), 635 (770). Elemental analysis calcd for $C_{86}H_{81}F_{19}N_4O_{36}$ [M, H_2O]: C, 49.01; H, 3.87; F, 17.13; N, 2.66; found: C, 48.88; H, 3.92; N, 2.56. MS (MALDI-TOF) m/z: calcd for $C_{86}H_{79}F_{19}N_4O_{35}Na$: 2111.41; found $[MHNa]^+$ 2112.41. HPLC: single peak at 21.62 min in 60–100% water–MeOH gradient, flow rate 0.7 ml min^{-1}, column SGX C18 250×4 mm (7 μm), recorded at 410 nm; the starting porphyrin **1** was eluted at 24.11 min.
17. Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *10*, 386–391.
18. Pasternack, R. F.; Collings, P. J. *Science* **1995**, *269*, 935–939.
19. Collings, P. J.; Gibbs, E. J.; Starr, T. E.; Vafek, O.; Yee, C.; Pomerance, L. A.; Pasternack, R. F. *J. Phys. Chem. B* **1999**, *103*, 8474–8481.
20. Král, V.; Schmidtchen, F. P.; Lang, K.; Berger, M. *Org. Lett.* **2002**, *4*, 51–54.
21. Huang, X.; Nakanishi, K.; Berova, N. *Chirality* **2000**, *12*, 237–255.
22. Rekharsky, M.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875–1917.
23. The feasibility of the electron transfer process can be evaluated using the Rehm–Weller equation: $\Delta G_{ET} = e[E_D^{ox} - E_A^{red}] - \Delta E_{00} + \omega$, where E_D^{ox} is the ground-state one-electron oxidation potential of porphyrin and E_A^{red} is the reduction potential of BQ ($E_A^{red} = -0.166$ V versus SCE) or AQS ($E_A^{red} = -0.634$ V versus SCE) (taken from Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637–1755). The energy ΔE_{00} of the excited singlet state of **2** is of 1.91 eV as obtained from the absorption and fluorescence spectra in buffer. We applied cyclic voltammetry to obtain the oxidation potential of **2**. Unfortunately, strong aggregation prevents this measurement in aqueous solutions. When recorded in methanol we only found an irreversible oxidation wave at 1.30 V versus SCE (a similar result was found in acetonitrile and dimethyl sulfoxide). We cannot calculate ΔG_{ET}, however, oxidative or reductive electron transfer processes occurring between water-soluble porphyrins and quinones or amino naphthalene have been described (Hoffman, M. Z.; Bolletta, F.; Moggi, L.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1989**, *18*, 219–543).