Structural studies of a non-covalently linked porphyrin–fullerene dyad

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X-ray structural and *ab initio* theoretical investigations of a non-covalently linked *meso*-tetraphenylporphyrinatozinc(II) and *N*-methyl-2-pyrid-4′-yl)-3,4-fullero-pyrrolidine complex is reported

Studies on non-covalently linked donor–acceptor dyads are of current interest because of their potential applications in constructing photovoltaic devices and also, to mimic the primary events of photosynthetic reaction centers.[1] Fullerenes as the electron acceptor in these dyads are particularly appealing because of their unique three-dimensional structure, excellent electron acceptor property, and a small re-organization energy involved in electron transfer reactions.[2] However, studies on non-covalently linked donor–fullerene dyads are limited[3] especially with respect to their crystal structures where no information is yet available even though a number of molecules including calixarenes, cyclodextrins, cyclotriveratrylene and porphyrins are known to form intermolecular complexes with fullerenes.[4] Fullerenes are also well-known to co-crystallize with a variety of molecules which include benzene, ferrocene, Pd_6, Cl_{12}, P_4 and S_8 moieties.[5]

Recently, the formation of stable, non-covalently linked dyads by axial coordination of functionalized C_{60} bearing a pyridine unit to zinc tetrapyrrole macrocycles have been reported.[3] In one such studied dyad, the kinetic analysis of the fullerene π-radical anion transient absorption resulting from irradiation of the ZnTPP-C_{60} dyad yielded a remarkable lifetime of several hundred microseconds with a quantum yield of about 0.14 for the separated radical pair.[3c] This enhanced lifetime of the radical pair was attributed to the diffusional splitting of the initial charge separated radical pair. Since the structural and thermodynamic factors play a crucial role in controlling the charge separation and charge recombination process, we, in the present study have performed X-ray structural analysis and *ab initio* calculations at B3LYP/3-21G(*) level on a non-covalently linked zinc porphyrin–fullerene dyad.

Slow evaporation of a solution mixture of CS_2, CH_2Cl_2 and *n*-heptane containing *meso*-tetraphenylporphyrinatozinc and *N*-methyl-2-(pyrid-4′-yl)-3-4-fulleropyrrolidine of 1 : 1 molar ratio yielded dark purple crystals that subsequently were handled in air. In agreement with the earlier reported solution structure,[3] the X-ray structural analysis of the crystals revealed a 1 : 1 stoichiometry.† Fig. 1 shows the structure of the porphyrin–fullerene complex while the packing diagram is shown in Fig. 2.

In the solid state structure, the zinc to axially coordinated pyridyl nitrogen distance is found to be 2.158(5) Å which compares with a 2.075(5) Å average distance of the porphyrin ring Zn–N bonds and a Zn–N distance of 2.147 Å reported earlier for an intramolecularly linked zinc porphyrin–pyridine adduct.[6] The edge-to-edge distance, that is, the closest distance between the porphyrin π-ring carbon (β-pyrrole) and the C_{60} carbon of the axially linked fulleropyrrolidine, is found to be 3.51 Å while the center-to-center distance between the porphyrin zinc ion and fullerene is ~9.53 Å. The distance between the closely located *meso*-phenyl ring (*meta* carbon) of the porphyrin macrocycle and the C_{60} spheroid is found to be 3.186 Å. In agreement with recent theoretical predictions,[7] the *N*-methylpyrrolidine ring on the fullerene spheroid revealed a *syn–trans* conformation. The 6,6 ring carbon atoms of the fullerene to which the pyrrolidine ring is attached is 0.33 Å away from the normal C_{60} spheroid. The porphyrin ring is also slightly ruffled (umbrella mode) with nearly 0.35 Å out-of-plane (defined by the four porphyrin ring nitrogens) displacement of the central zinc because of axial coordination.

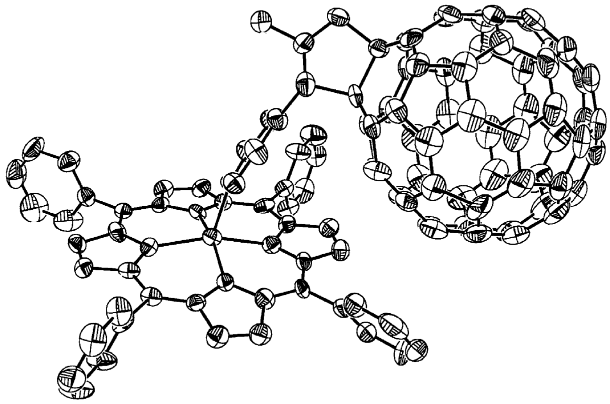

Fig. 1 Projection diagram of the axially coordinated *meso*-tetraphenylporphyrinato-zinc(II) and *N*-methyl-2-(pyrid-4′-yl)-3,4-fulleropyrrolidine complex with 50% thermal ellipsoids. The co-crystallized solvent, *n*-heptane and hydrogen atoms are not shown for clarity.

Additional inter-complex type interactions between the zinc porphyrin and the C_{60} unit that is not directly coordinated to the zinc but located on the other side of the porphyrin macrocycle have been observed in the crystal packing (Fig. 2). That is, the

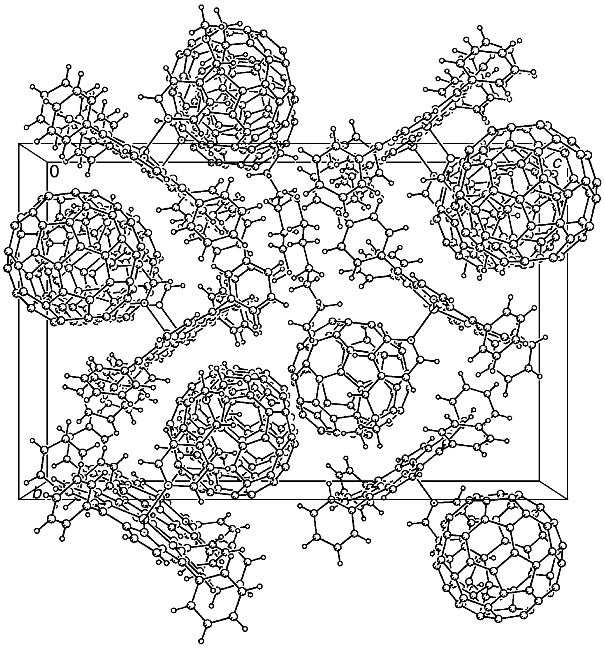

Fig. 2 Packing diagram of the investigated zinc porphyrin–C_{60} complex.

calculated inter-complex distances between the porphyrin ring atoms and C_{60} carbon are close to the calculated van der Waals distances. The central zinc to the closest C_{60} carbon is located at 3.228 Å while this distance between the porphyrin ring nitrogen to C_{60} carbon is 3.114 Å. The nearest porphyrin ring carbon (α-pyrrole) to the C_{60} spheroid carbon is 3.360 Å. These results indicate the existence of significant amounts inter-complex interactions in addition to the strong axial coordinate interactions in the investigated self-assembled supramolecular complex.

In order to further our understanding on the structure of this non-covalently linked dyad, *ab initio* calculations at B3LYP/3-21G(*) level by using Gaussian 98[8] have been performed. For this, first, both the starting compounds, tetraphenylporphyrinatozinc and *N*-methyl-2-(pyrid-4′-yl)-3,4-fulleropyrrolidine were fully optimized to a stationary point on the Born–Openheimer potential energy surface and allowed to interact. The geometric parameters of the dyad were obtained after complete energy minimization. In the calculated structure, the Zn–N distance of the axial coordination bond is found to be ~2.03 Å which is close to the average distance of the four Zn–N bonds (2.10 Å) of the porphyrin and that obtained in the crystal structure (2.074 Å). The center-to-center distance, that is, the distance between the central zinc and the center of the C_{60} spheroid, is found to be ~9.63 Å. The edge-to-edge distance, that is, the distance between the closest *meso*-carbon of the porphyrin ring and the C_{60} carbon, is ~5.17 Å while this distance between the closest β-pyrrole carbon and C_{60} spheroid carbon is ~4.69 Å. Generally, the tilting of the C_{60} unit towards the porphyrin ring is more in the crystal structure than that in the calculated structure, which may be a result of crystal packing. The calculated bond dissociation energy of the axial coordinate bond, that is, the energy difference between the dyad and the sum of the energies of individual zinc porphyrin and fulleropyrrolidine units, is found to be 28.21 kcal mol^{-1} and this compares well with a value of 26.91 kcal mol^{-1} obtained experimentally in 1,2-dichlorobenzene.[3d]

In summary, this paper presents the first X-ray structure of a non-covalently linked porphyrin–fullerene donor–acceptor dyad. The structure agrees well with the theoretically calculated one and the earlier reported spectroscopic studies. Further studies along this line are in progress.

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Notes and references

† *Crystal data for zinc porphyrin–C_{60} complex*: Empirical formula, $C_{119}H_{54}N_6Zn$, M = 1633.05, $P2_12_12_1$, a = 13.2914(5), b = 19.1411(7), c = 29.532(1) Å, V = 7513.2(5) Å^3, Z = 4, μ = 0.393 mm^{-1}, T = 218(2) K. The final residual values were R(F) = 9.2% for 7953 observed reflections [$I > 2\sigma(I)$] and $wR(F^2)$ = 15.4%; s = 0.98 for all data. CCDC 155575. See http://www.rsc.org/suppdata/cc/b0/b009528c/ for crystallographic files in .cif format.

1 *Molecular Electronic Devices*, eds. F. L. Carter, R. E. Siatowski and H. Woltjen, North Holland, Amsterdam, 1999; V. Balzani and F. Scandola, in *Comprehensive Supramolecular Chemistry*, Vol. 10, ed. D. N. Reinhoudt, Pergamon–Elsevier, Oxford, 1996, pp. 687–746; M. D. Ward, *Chem. Soc. Rev.*, 1997, **26**, 365.

2 D. M. Guldi, *Chem. Commun.*, 2000, 321.

3 (*a*) F. D'Souza, G. R. Deviprasad, M. S. Rahman and J.-P. Choi, *Inorg. Chem.*, 1999, **38**, 2157; (*b*) N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi and J.-F. Nierengarten,. *New. J. Chem.*, 1999, 77; (*c*) T. Da Ros, M. Prato, D. Guldi, E. Alessio, M. Ruzzi and L. Pasimeni, *Chem. Commun.*, 1999, 635; (*d*) G. R. Deviprasad, M. E. Zandler and F. D'Souza, in *Fullerenes 2000: Electrochemistry and Photochemistry*, ed. S. Fukuzumi, F. D'Souza and D. M. Guldi, *Proc. Electrochem. Soc.*, 2000, **8**, 182.

4 J. L. Atwood, L J. Barbour, C. L. Raston and I. B. N. Sudria, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 981; Z. Yoshida, H. Takekuma, S. Takekuma and Y. Matsubara, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1597; J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1994, **116**, 10 346; A. L. Balch, V. J. Catalasono, J. W. Lee and M. M. Olmstead, *J. Am. Chem. Soc.*, 1992, **114**, 5455; P. D. W. Boyd, M. C. Hodgson, C. E. F. Richard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 1999, **121**, 10 487; M. M. Olmstead, D. A. Costa, K. Maitra, B. C Noll, S. L. Phillips, P. M. Van Calcar and A. L. Balch, *J. Am. Chem. Soc.*, 1999, **121**, 7090; D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2000, **122**, 10 704.

5 A. L. Balch, J. W. Lee, B. C. Noll and M. M. Osmstead, *J. Chem. Soc., Chem. Commun.*, 1993, 56; J. D. Cram, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. M. R. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764; M. M. Olmstead, A. S. Ginwalla, B. C. Noll, D.S. Tinti and A. L. Balch, *J. Am. Chem. Soc.*, 1996, **118**, 7737; M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123 and references cited therein.

6 M. A. Bobrik and F. A. Walker, *Inorg. Chem.*, 1980, **19**, 3383.

7 F. D'Souza, M. E. Zandler, G. R. Deviprasad and W. Kutner, *J. Phys. Chem. A*, 2000, **104**, 6887.

8 *Gaussian 98* (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian, Inc., Pittsburgh PA*, 1998.