

Unexpectedly large binding constants of azulenes with fullerenes†

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Received (in Cambridge, UK) 28th November 2007, Accepted 17th December 2007

First published as an Advance Article on the web 14th January 2008

DOI: 10.1039/b718392e

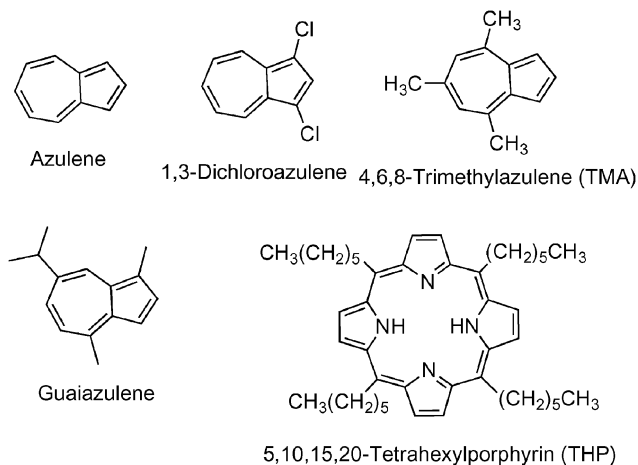
In spite of having small π -conjugation systems, azulenes show large binding constants (10^4 – 10^5) to C_{60} and C_{70} , which are larger than those of monoporphyrins and alternant aromatic hydrocarbons.

Fullerene-based supramolecular complexes have attracted much attention from viewpoints of the separation of fullerenes^{1–5} and the construction of photosynthetic systems and photonic devices.^{6,7} In light of stability of the complexes, host molecules with concave shapes have been designed—such as calixarenes,^{8,9} resorcarenes,^{10,11} cyclodextrins¹² and carbon nanorings.^{13–15} However, it has been recognised that concave–convex interaction is not always necessary¹⁶ to realise a highly stabilised complex since the first finding of the close contact (~ 2.75 Å) between a curved π -surface of fullerene and a flat π -surface of porphyrin in 1997.¹⁷ In effect, porphyrin dimers,^{18–23} tetramer²⁴ and hexamer,²⁵ and even monoporphyrins^{26,27} show comparable or even larger binding constants to fullerenes than the concave host molecules mentioned above. Such a non-classical strong π – π interaction has been known only in the fullerene–porphyrin complexes so far. In continuation of our efforts to investigate fullerene–porphyrin^{26–29} and carbon nanotube–porphyrin^{30,31} ensembles, we found another example of the strong flat– π –curved– π interaction between fullerenes and azulenes having a much smaller π -conjugation system than porphyrins.

Azulenes^{32–34} and 5,10,15,20-tetrahexylporphyrin (THP)³⁵ shown in Scheme 1 were prepared according to the reported methods. Binding constants between fullerenes and azulenes ($K_{C_{60}}$ and $K_{C_{70}}$) were determined by Stern–Volmer plots on the basis of the spectral changes in fluorescence upon the titration of fullerene solution to the azulene solution (Fig. 1 and Fig. S1–S7 in ESI†).‡ All the plots exhibit straight lines with >0.99 correlation coefficient, clearly indicating the 1 : 1 stoichiometry of azulenes and fullerenes in the complex. The binding constants thus determined are summarised in Table 1.

Azulenes show large binding constants (5.7×10^4 – 1.7×10^5 $\text{dm}^3 \text{mol}^{-1}$), and each azulene compound exhibits similar

affinity to C_{60} and C_{70} (entries 1–4 in Table 1). As compared with the host molecules reported so far, the binding constants of azulenes are comparable to or larger than those of bridged calixarenes,^{36,37} azacalixpyridines,³⁸ cyclotrimeratrylenes,^{39,40} and di- and tetraporphyrins.^{18,24} However, the binding constants of azulenes are smaller than those of the well-designed host molecules such as carbon nanorings,^{13,41} cyclic diporphyrins^{22,23} and hexaporphyrins.²⁵ In spite of being much smaller in size, azulenes exhibit larger binding constants than



Scheme 1 Structures of azulenes and porphyrin (THP) used for the determination of binding constants with fullerenes.

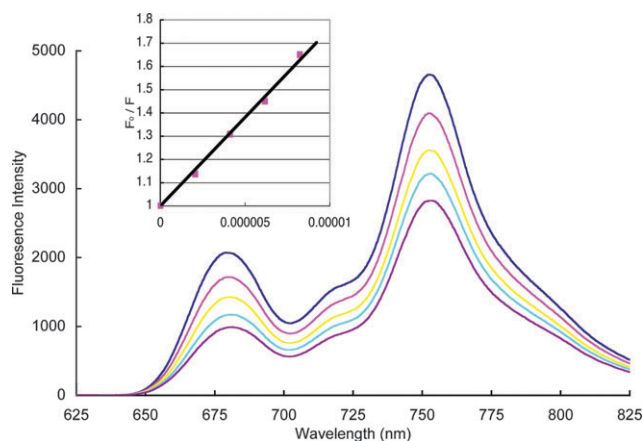


Fig. 1 Fluorescence spectra of azulene ($8.46 \times 10^{-5} \text{ mol dm}^{-3}$) in the presence of C_{60} (0 – $8.23 \times 10^{-6} \text{ mol dm}^{-3}$) in toluene at 298 K ($\lambda_{\text{exc}} = 351 \text{ nm}$, $\lambda_{\text{em}} = 753 \text{ nm}$). Inset: Stern–Volmer plot (correlation coefficient: 0.995).

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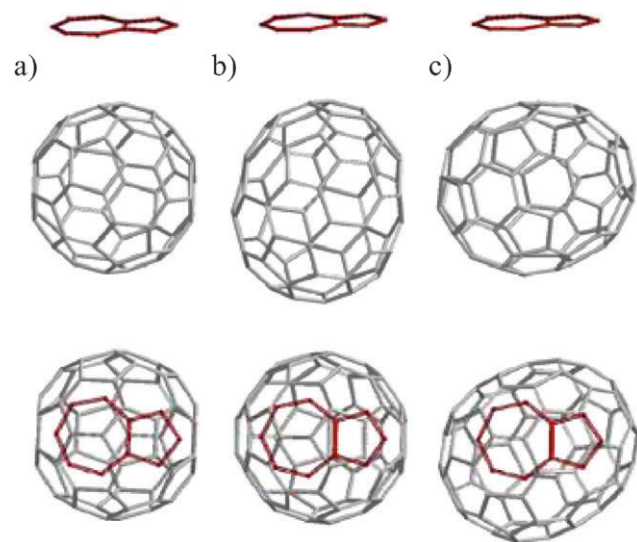
† Electronic supplementary information (ESI) available: Fluorescence spectra and Stern–Volmer plots for the determination of the binding constants of azulenes with C_{60} and C_{70} (Fig. S1–S7), and procedure and conditions in theoretical calculations. See DOI: 10.1039/b718392e

Table 1 Binding constants of azulenes and porphyrins with C_{60} ($K_{C_{60}}/\text{dm}^3 \text{mol}^{-1}$) and C_{70} ($K_{C_{70}}/\text{dm}^3 \text{mol}^{-1}$) in toluene at 298 K

Entry	Donor	$K_{C_{60}}/\text{dm}^3 \text{mol}^{-1}$	$K_{C_{70}}/\text{dm}^3 \text{mol}^{-1}$	$K_{C_{70}}/K_{C_{60}}$
1	Azulene	7.6×10^4	7.9×10^4	1.0
2	1,3-Dichloro-azulene	6.7×10^4	7.3×10^4	1.1
3	TMA	1.7×10^5	1.5×10^5	0.88
4	Guaiazulene	5.7×10^4	8.8×10^4	1.5
5	THP	1.7×10^3	1.5×10^4	8.8

that of the monoporphyrin THP (entry 5).²⁶ For the ratio of $K_{C_{70}}/K_{C_{60}}$, azulenes show almost no difference in binding constants with C_{60} and C_{70} ($K_{C_{70}}/K_{C_{60}} \approx 1$), whereas THP shows a much higher affinity towards C_{70} than C_{60} ($K_{C_{70}}/K_{C_{60}} = 8.8$). Noteworthy is that naphthalene, a structural isomer of azulene, and other alternately conjugated hydrocarbons were reported to show much lower binding constants to fullerenes ($1\text{--}500 \text{ dm}^3 \text{ mol}^{-1}$).^{42,43}

In order to gain insight into the unexpected binding behavior of azulenes with fullerenes, we calculated the energy-minimised structures of the complexes (Fig. 2) and the enthalpy of the association (Table 2) by *ab initio* Hartree–Fock method using STO 3-21G* basis set (ESI†). Interestingly, the end-on structure of the C_{70} –azulene complex is more stable than its side-on structure (entry 1 in Table 2). The low selectivity of azulenes ($K_{C_{70}}/K_{C_{60}} \approx 1$) can be accounted for by the lack of structural difference between azulene– C_{60} and azulene– C_{70} (end-on) shown in the top-views of Fig. 2(a) and (b), respectively. The more stable end-on structure of C_{70} –azulene is in marked contrast with the cases of porphyrins, where side-on is more stable (entry 2 in Table 2).^{18,22,26,27,44} In the fullerene–porphyrin complexes, dispersion forces are reported to be dominant²⁶ and, hence, C_{70} and porphyrins prefer to have as large a contact area as possible. This is probably because C_{70} is prone to have a side-on orientation to the porphyrin plane.^{18,22,26,27,44} On the other hand, azulene pos-

**Fig. 2** Side- and top-views of energy-minimised structures of azulene with (a) C_{60} , (b) C_{70} (end-on) and (c) C_{70} (side-on). Hydrogen atoms are omitted for clarity.**Table 2** Enthalpy of association (ΔH^0) of azulene and THP with C_{60} and C_{70} (end-on and side-on structures)

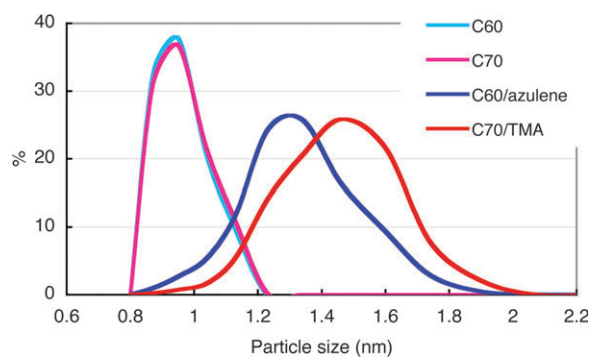
Entry	Donor	$\Delta H^0/\text{kcal mol}^{-1}$		
		C_{60}	C_{70} (end-on)	C_{70} (side-on)
1	Azulene	-0.15	-0.041	0.072
2	THP	5.8	5.2	2.3

sesses both electron donating and accepting character in the five- and seven-membered rings, respectively.⁴⁵ In the energy-minimised complex structure of C_{70} and azulene shown in Fig. 2(b), electron-rich 6–6 and electron-deficient 6–5 junctures⁴⁶ in the C_{70} face the electron-deficient seven-membered and electron-rich five-membered rings in azulene, respectively (top-view in Fig. 2(b)). This implies an existence of electrostatic interaction between C_{70} and azulene, making the end-on orientation of C_{70} more stable.

Complexation of azulenes with fullerenes was successfully observed by particle size analysis using dynamic light scattering as shown in Fig. 3. The median sizes of C_{60} and C_{70} are $\sim 1.0 \text{ nm}$, which corresponds to their sizes (including π -electrons). After complexation with azulene and TMA, their median sizes increased to ~ 1.3 and $\sim 1.4 \text{ nm}$, respectively. The difference in these sizes before and after complexation, 0.3–0.4 nm, corresponds to the π -electron thickness of the azulenes, supporting the above-mentioned results of very high binding constants and 1 : 1 stoichiometry between fullerenes and azulenes. This may be the first example to track the complexation behaviour by particle size analysis. This facile method may give us information about the occurrence of complexation and, if so, of the size and stoichiometry of the complex.

In conclusion, azulenes show very high and similar affinity to C_{60} and C_{70} . Such binding behaviour of azulene is in contrast with that of porphyrins, probably due to the different dominating interactions; electrostatic force for azulenes and dispersive force for porphyrins.

We thank Dr Mitsumi Uchida (Osaka Prefecture University) for proof-reading the manuscript and Mr. Masahiro Suzuki (Nikkiso Co., Ltd.) for helpful suggestion in particle size analysis of fullerenes. S. B. acknowledges Japan Society of Promotion of Science (JSPS) for providing a post-doctoral fellowship to him (No. P05389). This work was supported by Grant-in-Aid for Scientific Research (No. 17 05389) from

**Fig. 3** Particle size distribution of C_{60} , C_{70} , C_{60} –azulene and C_{70} –TMA.

JSPS and Industrial Technology Research Grant Program in 2005 from New Energy and Industrial Technology Development Organisation (NEDO) of Japan.

Notes and references

‡ The binding constants were not able to be determined by NMR and UV-Vis spectra. In the NMR spectra, the peak shifts are too small in both ^1H and ^{13}C NMR even under low-temperature conditions. In the UV-Vis spectra, the largest absorption of azulene at around 340 nm also contains absorption from the fullerenes.

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