Electric Supporting Information

Unexpectedly Large Binding Constants of Azulenes with Fullerenes**

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Equipments

Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer. Particle size analysis was performed on a Nanotrac UPA-UT151 (Microtrac Inc.).

Theoretical Calculation

Elucidation of enthalpies of association (ΔH^0) for both fullerene complexes of azulene and porphyrin were performed by *ab initio* Hartree-Fock method using Slater type orbital basis set. Before the calculation, the geometry of the complexes as well as individual host and guest was optimized by *ab initio* Hartree-Fock method using 3-21G* basis set. The BSSE corrections were incorporated before start of each calculation.

Determination of Binding Constants of Azulenes with Fullerenes

The binding constants were determined by fluorescence spectra shown below (Figs. S1 - S7).



Fig. S1 Fluorescence Spectra (λ_{ex} = 341 nm) of azulene (8.46 x 10⁻⁵ mol/dm³) in the presence of C₇₀ (0 – 8.15 x 10⁻⁶ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot (λ_{em} = 753nm, correlation coefficient: 0.994) (b).



Fig. S2 Fluorescence Spectra (λ_{ex} = 344 nm) of 1,3-dichloroazulene (2.55 x 10⁻⁵ mol/dm³) in the presence of C₆₀ (0 – 9.26 x 10⁻⁶ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot (λ_{em} = 753nm, correlation coefficient: 0.997) (b).



Fig. S3 Fluorescence Spectra (λ_{ex} = 344 nm) of 1,3-dichloroazulene (2.55x 10⁻⁵ mol/dm³) in the presence of C₆₀ (0 – 1.164 x 10⁻⁵ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot ((λ_{em} = 753 nm, correlation coefficient: 0.995) (b).



Fig. S4 Fluorescence Spectra (λ_{ex} = 350 nm) of 4,6,8-trimethylazulene (1.96 x 10⁻⁵ mol/dm³) in the presence of C₆₀ (0 – 2.52 x 10⁻⁵ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot ((λ_{em} = 392 nm, correlation coefficient: 0.997) (b).



Fig. S5 Fluorescence Spectra (λ_{ex} = 350 nm) of 4,6,8-trimethylazulene (1.96 x 10⁻⁵ mol/dm³) in the presence of C₇₀ (0 – 2.00 x 10⁻⁵ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot ((λ_{em} = 392 nm, correlation coefficient: 0.995) (b).



Fig. S6 Fluorescence Spectra (λ_{ex} = 351 nm) of guaiazulene (1.48 x 10⁻⁵ mol/dm³) in the presence of C₆₀ (0 – 6.16 x 10⁻⁶ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot ((λ_{em} = 785 nm, correlation coefficient: 0.999) (b).



Fig. S7 Fluorescence Spectra (λ_{ex} = 351 nm) of guaiazulene (1.48 x 10⁻⁵ mol/dm³) in the presence of C₇₀ (0 – 8.47 x 10⁻⁶ mol/dm³) in toluene at 298K (a) and Stern-Volmer plot ((λ_{em} = 785 nm, correlation coefficient: 0.999) (b).