Supermolecular Association Behavior of a Strong C₆₀ Receptor with Conjugated Pentacene and Tetrathiafulvalene Moieties in Solution and Solid State

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Electronic Supplementary Information

(ESI)

General methods. Synthesis used chemicals and solvents that were reagent grade purchased from Aldrich, Acros Chemical Co.. Unless otherwise indicated, all starting materials were used without further purification. The silica gel for column chromatography was purchased from JIYIDA Silica Gel Corp. in Qing Dao (200–300 mesh). The ¹H NMR spectra were recorded with Bruker Advance 400 spectrometer. UV-vis spectra were recorded in a Jasco V-570 spectrophotometer.

Compound 1. Triethyl phosphite (10 mL) was degassed, heated to 130°C, and stirred under argon, and then pentacene-6,13-dione (0.46g, 1.5mmol) was added. Over the next 3h 5,6-dihydro[1,3]dithiolo-[4,5-b][1,4] - dithiine-2-thione (1.35g, 6mmol) was added as a solid in small portions against a positive pressure of argon. The reaction mixture turned dark red-brown, and the formation of 1 was monitored using TLC. After completing addition of 5,6-dihydro[1,3]dithiolo-[4,5-b][1,4]-dithiine-2 - thione, the mixture was stirred for another 30 min at 130°C and then cooled to 0°C, and dichloromethane was added. The precipitate was filtered, washed with dichloromethane, dried in vacuo, and column chromatographed to give 1 as a yellow powder (0.66g, 67%). Yellow prisms were obtained by recrystallization in dichloromethane.

UV–vis spectral titration of exTTF 1 with C₆₀

Typical procedures for spectroscopic titration and evaluation of association constants K_a : Aliquots of a PhCl solution of C_{60} (1 × 10⁻⁴ M)

were added to a PhCl solution of **1** (2.0 × 10⁻⁵ M), and the mixture was subjected to UV–vis spectroscopy at 25 °C. Each spectrum was corrected with a dilution factor and background subtraction. The difference in absorbance (ΔA) of **1** in the presence (A; A_∞ = A at infinite [1]) and absence (A₀) of C₆₀ was measured at 427 nm, and the data were plotted against [C₆₀]. The UV-vis spectral change upon titration exhibited isosbestic points, indicating that each **1** binds independently with a C₆₀ unit. Thus, association constant K_a was evaluated by non-linear curve fitting using the equation: $\Delta A = \Delta A_{\infty}((1 + K_a[G] + K_a[H]_0) - ((1 + K_a[G] + K_a[H]_0)^2 - 4 K_a^2[H]_0[G])^{0.5}) / (2K_a[H]_0)$, Where $\Delta A = A - A_0$, $\Delta A_{\infty} = A_{\infty} - A_0$, [G] is [fullerene], [H]_0 = [**1**].



Figure S1. Job's plot for **1** upon decreasing molar fraction of C_{60} at a fixed total concentration of 1.25 x 10⁻⁵ M. Note the maximum at X=0.5.



Figure S2. Partial ¹H NMR spectra (400 MHz, 298 K, $CDCl_3/CS_2$) of 1 upon addition of C_{60} .



Figure S3. Spectral changes in a UV-vis titration experiment of 1 upon addition of C_{70} in PhCl at room temperature.



Figure S4. Partial ¹H NMR spectra (400 MHz, 298 K, $CDCl_3/CS_2$) of 1 upon addition of C_{70} .