Supporting Information

Weighting non-covalent forces in the molecular recognition of C_{60}. Relevance of concave-convex complementarity

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1. Experimental Section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium coated Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on a Bruker Avance 300 (1H: 300 MHz; 13C: 75 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. Electrospray Ionization Mass Spectra (ESI-MS) were recorded on a HP1100MSD spectrometer.

(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methanol (exTTF methylene alcohol) was synthesised as described by G. J. Marshallsay and M. R. Bryce in *J. Org. Chem.* **1994**, *59*, 6847-6849 and showed identical spectroscopic data to those reported therein.

2,2'-(2-(hydroxymethyl)anthracene-9,10-diylidene)dimalononitrile (TCAQ methylene alcohol) was synthesised as previously reported by our group in *J. Org. Chem.* **2000**, *65*, 5728-5738 and was satisfactorily characterized by standard spectroscopic techniques.

2-(hydroxymethyl)anthracene-9,10-dione (AQ methylene alcohol) was purchased from Aldrich and used without further purification.

(hydroxymethyl)tetrathiafulvalene was synthesised as described by J. Garín et al. in *Synthesis* **1994***, 5,* 489-93 and showed identical spectroscopic data to those reported therein.

The synthesis and characterization of **receptor 1** was reported by us in *J. Am. Chem. Soc.* **2006**, *128*, 7172-7173.

Receptor 4 was prepared as described by the group of M. R. Bryce in *J. Mater. Chem.* **1998**, *8*, 1361-1372 and was satisfactorily characterized by standard spectroscopic techniques.

Typical procedure for the synthesis of receptors 2 and 3.

To a suspension of the corresponding methylene alcohol (0.123 g, 0.33 mmol) and 4-dymethylaminopyridine (0.050 g, 0.41 mmol) in 5 mL of dry CH_2Cl_2, a solution of isophthaloyl chloride (0.033 g, 0.16 mmol) in 10 mL of dry CH_2Cl_2 was added dropwise over a period of 2 hrs using motor-driven syringe pumps. The resulting solution was allowed to stir at room temperature for 2-16 hrs, then concentrated under reduced pressure and purified by flash chromatography on silica gel, to afford pure compounds **2** and **3** 45 % and 62 %, respectively.

Receptor 2. Mp 190-194 ˚C; ^{1}H NMR ($CDCl_3$) δ 8.80 (brt, 1H), 8.35-8.22 (m, 10H), 7.82 (d, J = 1.4 Hz, 2H), 7.79-7.72 (m, 8H), 7.61 (t, J = 7.8 Hz, 1H), 5.55 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 165.6, 160.3, 160.1, 141.5, 135.1, 133.0, 131.8, 131.5, 131.1, 130.5, 130.3, 129.5, 129.4, 128.1, 127.0, 113.4, 83.9, 83.7, 65.7. ESI-MS *m/z*: calcd. for $C_{50}H_{22}N_8O_4$ [M] = 798.18; found [M+H$^+$] = 799.4.

Receptor 3. M.p. 150-153 °C; ^{1}H NMR ($CDCl_3$) δ 8.77 (brt, 1H); 8.40-8.28 (m, 8H); 7.92 (dd, *J* = 1.4 Hz, *J* = 7.9 Hz, 2H) –7.83 (m, 6H); 7.61-7.56 (t, *J* = 7.9 Hz, 1H); 5.58 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 182.8, 165.7, 142.5, 134.3, 134.2, 133.8, 133.13, 130.8, 128.7, 127.8, 127.3, 126.3, 65.8. MS *m/z*: calcd. for $C_{38}H_{22}O_8$ [M] = 606.13; found [$M+H^+$] = 607.2

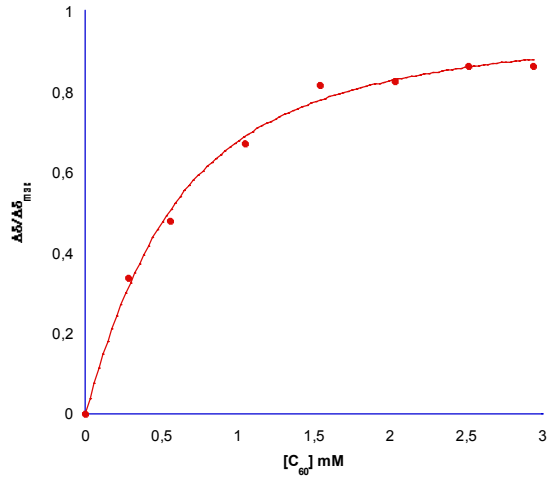
2. Titration Experiments

Binding constants K_a for receptors **1-3** were evaluated from the changes of the chemical shifts of a suitable proton as a function of C_{60} concentration applying a non-linear curve-fitting using the equation shown below (eq. 1):

$$\Delta\delta/\Delta\delta_{max} = (K_aX - K_aY - 1 + ((K_aX + K_aY +1)^2 - 4\,K_a^2XY)^{1/2})/((\,1+ K_a\,X - K_aY + ((\,K_aX + K_aY +1)^2 - 4\,K_a^2XY)^{1/2}))$$

Receptor **1**

Eight solutions containing receptor **1** 0.5 mM and C_{60} 0, 0.28, 0.56, 1.0, 1.54, 2.03, 2.52 and 2.94 mM, repectively in $CDCl_3/CS_2$ $(1/1)_{v/v}$ were prepared. Care was taken to limit exposure of the solutions to light. The ^{1}H NMR spectrum was recorded for each solution.



K_a(**1**) = (2.875 ± 0.15) × 10^3 M^{-1}

R = 0.997

A duplicate of this experiment led to the following values:

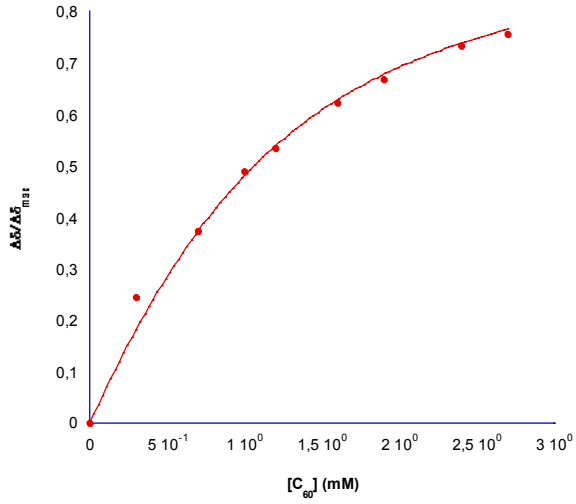
K_a(**1**) = (3.13 ± 0.199) × 10^3 M^{-1}

R = 0.997

Average value: K_a(**1**) = 3.00 × 10^3 M^{-1}

Receptor **2**

2.2 mg of **2** were dissolved in 3 mL of $CDCl_3/CS_2$ 1:1 to give a 0.9 × 10^{-3} M stock solution**.** 500 µL of this solution were then titrated with 50, 130, 200, 300, 500, 650, 1250 and 1800 µL of a solution 3.4 × 10^{-3} M in C_{60} and 0.9 × 10^{-3} M in **2** in $CDCl_3/CS_2$ 1:1 (constant concentration of **2**). The ^{1}H NMR spectrum was recorded after each addition.



K_a(**2**) = (1.687 ± 0.082) × 10^3 M^{-1}

R = 0.996

A duplicate of this experiment led to the following value:

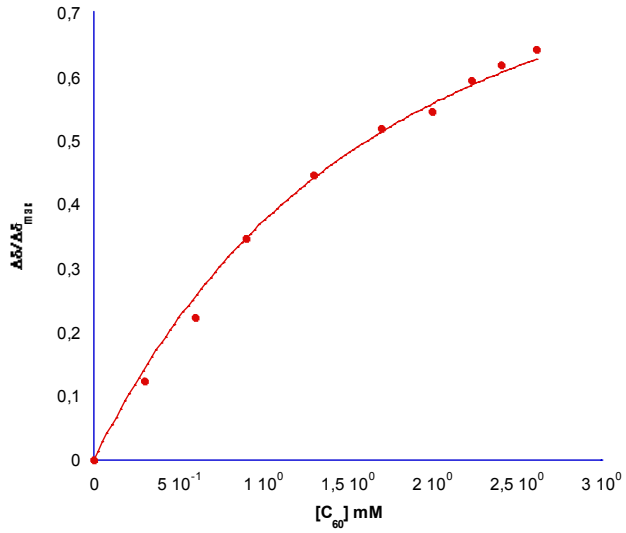
K_a(**2**) = (1.388 ± 0.044) × 10^3 M^{-1}

R = 0.998

Average value: K_a(**2**) = 1.54 × 10^3 M^{-1}

Receptor **3**

1.1 mg of **3** were dissolved in 3 mL of $CDCl_3/CS_2$ 1:1 to give a 6.0 × 10^{-4} M stock solution**.** 500 µL of this solution were then titrated with 50, 100, 200, 300, 500, 700, 1000, 1300, and 1800 µL of a solution 3.4 × 10^{-3} M in C_{60} and 6.0 × 10^{-4} M in **1** in $CDCl_3/CS_2$ 1:1 (constant concentration of **1**). The ^{1}H NMR spectrum was recorded after each addition.



K_a(**3**) = (726 ± 15) M^{-1}

R = 0.9983

A duplicate of this experiment led to the following value:

K_a(**3**) = (849 ± 25) M^{-1}

R = 0.992

Average value: K_a(**3**) = 7.90 × 10^2 M^{-1}

3. Theoretical Calculations

All theoretical calculations were carried out within the density functional theory (DFT) approach by using the C.02 revision of the Gaussian 03 suite of programs.[1] Calculations were performed making use of Becke's "half-and-half" functional, BH&H.[2] This is an *ad hoc* mixture of exact Hartree-Fock (HF) and local density approximation (LDA) exchange, coupled with Lee, Yang, and Parr's (LYP) expression[3] for the correlation energy. The attractiveness of the BH&H functional to calculate supramolecular associations is that it successfully reproduces the results of highly accurate post-HF methods for π-stacked complexes.[4-7] Waller et al.[4] found that the BH&H functional provides a binding energy for the archetypal

parallel-displaced benzene dimer in good agreement with the best available high-level computational methods. Truhlar et al.[6] have recently reported a very comprehensive study of a large database of non-covalent interacting systems using different functionals and concluded that "the BH&H functional gives good performance for dispersion-dominated interactions". A similar conclusion is stated by Hobza et al.[8] in a very recent study on small peptides for which the interaction is dominated by dispersion forces.

Complexation binding energies were first obtained by fully optimising the geometry of both the isolated components (receptor and C_{60}) and the supramolecular complex using the 6-31G** basis set.[8] Binding energies were afterwards recalculated using the more extended 6-31+G** basis set,[9] which includes diffuse functions on the heavy atoms, and the minimum-energy 6-31G**-optimised geometries. The basis set superposition error (BSSE) was calculated using the counterpoise correction approach.[10] The BSSE is a spurious contribution to the interaction energy arising from the improved description of the molecular fragment A in the complex A•••B due to the assistance of the basis set located in fragment B, and vice versa. The counterpoise method corrects the interaction energy of the complex A•••B by computing the energies of the isolated fragments A and B with exactly the same basis set (both in number and location) as used to compute the complex A•••B. Binding energies are strongly dependent on the basis set used to compute them. BH&H/6-31G** calculations provided binding energies of –20.4 kcal mol^{-1} for **1**•C_{60}, –19.6 kcal mol^{-1} for **2**•C_{60}, and –19.7 kcal mol^{-1} **3**•C_{60}, that are similar to those obtained with the more extended 6-31+G** basis set (–19.6, –18.1 and –18.9 kcal mol^{-1}, respectively). However, the 6–31G** basis set led to significantly lower binding energies (–9.8, –9.4 and –10.4 kcal mol^{-1}, respectively) than those obtained with the 6-31+G** basis set (–13.4, –12.5 and –13.1 kcal mol^{-1}, respectively) when the correction for the BSSE error is included. This difference is due to the well kwown fact that smaller basis sets give rise to larger BSSE errors.

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