Supplementary Material (ESI) for Chemical Communications

Supporting Information

Preferential Separation of Fullerene[84] From Fullerene Mixtures by Encapsulation

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Materials and Methods:

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled using conventional methods[1] or using a Solvent Purification System (SPS).

NMR spectra were performed on Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) and 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) Ultrashield spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm, and are referred to the residual peak of the solvent. UV titrations were done in a Shimadzu UV-2401PC UV-Vis spectrophotometer with a thermostated (7–60 ºC) sample holder (optical range from 190 to 900 nm).

High performance liquid chromatography (HPLC) analyses of the fullerene mixtures were carried out on an Agilent Technologies 1200 Series apparatus using a Nacalai Tesque Cosmosil Buckyprep M column (4.6x250mm) purchased from SESres, with diode array detection (monitoring signal at 290 nm).

HPLC grade solvents were purchased from Carlo Erba and were used without further purification.

The mobile phase used was toluene/methanol (80:20) at 30 °C and flow rate 1mL/min.

Calibration of the system was carried out using concentrations of pure C_{60} (purchased from CYMIT QUIMICA S.L), C_{70} (purchased from Sigma Aldrich) and C_{84} (purchased from BuckyUSA) (Table S1). All of them were dissolved in 1-chloronaphthalene (purchased from Sigma-Aldrich).

[1] D. D. Perrin, W. L. F. Amarego, D. R. Perrin, *Purification of Laboratory Chemicals*, *2nd ed.*, Pergamon Press, Oxford, **1980**.

Table S1: Standard concentrations

Standards	Concentrations [M]		
	C_{60}	C_{70}	C_{84}[2]
1	$9.77x10^{-4}$	$1.04x10^{-3}$	$1.78x10^{-4}$
2	$7.67x10^{-4}$	$7.96x10^{-4}$	$1.48x10^{-4}$
3	$4.89x10^{-4}$	$5.22x10^{-4}$	$8.92x10^{-5}$
4	$2.44x10^{-4}$	$2.61x10^{-4}$	$4.46x10^{-5}$
5	$1.22x10^{-4}$	$1.30x10^{-4}$	$2.23x10^{-5}$
6	$6.11x10^{-5}$	$6.52x10^{-5}$	$1.12x10^{-5}$
7	$3.05x10^{-5}$	$3.26x10^{-5}$	$5.58x10^{-6}$
8	$1.53x10^{-5}$	$1.63x10^{-5}$	$2.79x10^{-6}$
9	$7.63x10^{-6}$	$8.15x10^{-6}$	$1.39x10^{-6}$
10	$3.82x10^{-6}$	$4.08x10^{-6}$	$6.97x10^{-7}$
11	$1.91x10^{-6}$	$2.04x10^{-6}$	$3.49x10^{-7}$
12	$9.54x10^{-7}$	$1.02x10^{-6}$	$1.74x10^{-7}$

The respective linear regressions are illustrated below taking into account outlier points after analysing the residuals[3]:

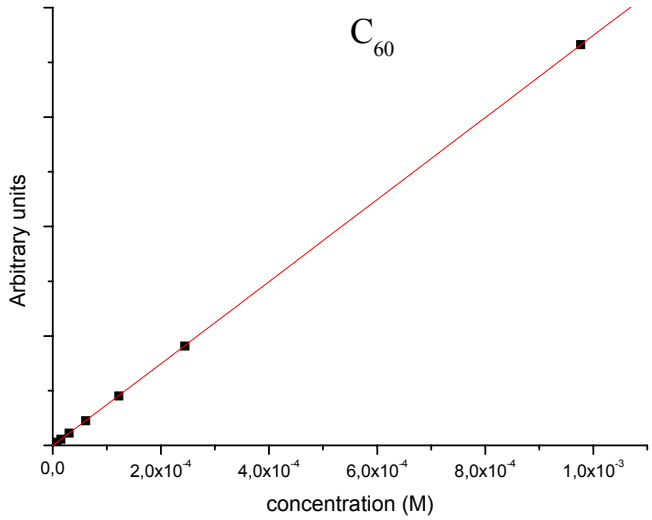

Figure S1: C_{60} calibration curve

[2] Concentrations of C_{84} below $5.58x10^{-06}$ M are not quantifiable by UV.
[3] Standards 2 and 3 of C_{60} and C_{70} have been eliminated.

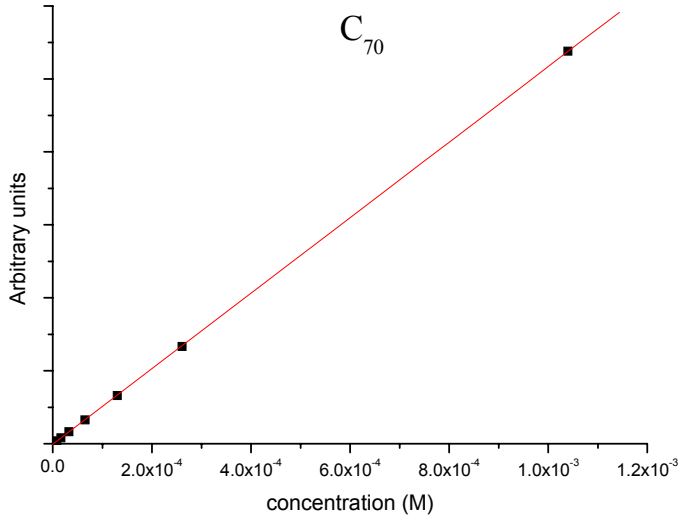

Figure S2: C_{70} calibration curve

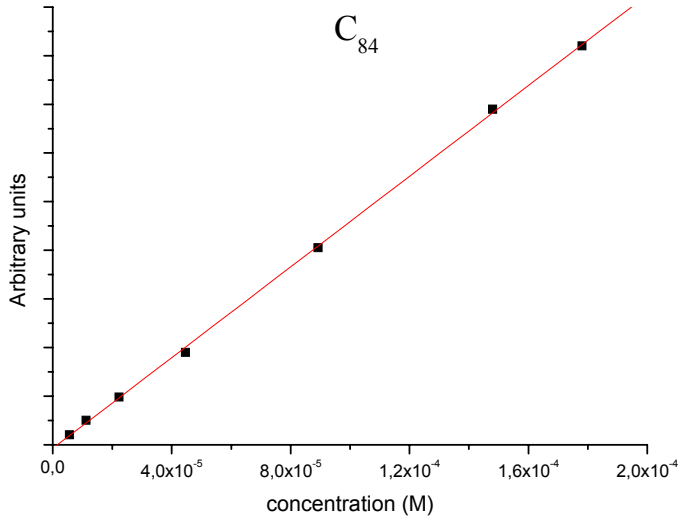

Figure S3: C_{84} calibration curve

Table S2: Linear regression values and confidence intervals[4].

	Slope	±	Intercept	±	R^2
C_{60}	$1.87x10^{+7}$	$2.72x10^{+4}$	-11.0	8.74	0.999998
C_{70}	$2.58x10^{+7}$	$6.27x10^{+4}$	-25.1	21.53	0.999996
C_{84}	$9.29x10^{+6}$	$2.08x10^{+5}$	-13.48	19.95	0.9996

C_{60}, C_{70} and C_{84} response is interpolated through the respective linear regression to obtain the final concentrations.

[4] C_{60} and C_{70} confidence intervals at a level of 95% (t=2.31). C_{84} confidence intervals at a level of 95% (t=2.57). Information extracted from *Statistics for Analytical Chemistry,* J.C Miller, J.N Miller, 1988.

Extractions Procedure and HPLC Samples Preparation. Compound **1** was dissolved in THF and the solution was added over a solid fullerene mixture, then THF was added to the mixture to complete the final volume (see table S3). The mixtures were stirred overnight. No sonication or heat was used during the extraction. The resulting suspension was filtered. To 2 mL of the solution containing the $\mathbf{1}_2$:fullerene complexes, 10 μL of TFA were added and solvent was then removed. The solid residue was redissolved in 0.5 mL of carbon disulphide and injected into the HPLC column. Compound **1** remains solid after addition of CS_2, allowing an easy recovery of the receptor, which can be reused.

Table S3: Extraction conditions

Entry	1[a]	Fullerite (mg)	1 (mg)	THF (mL)
1	0%	7,80	0,00	2,50
2	1%	7,81	0,08	2,44
3	3%	7,49	0,22	2,51
4	5%	8,37	0,42	2,51
5	10%	8,20	0,82	2,50
6	15%	8,16	1,22	2,50
7	20%	8,26	1,65	2,50
8	40%	8,13	3,25	2,50
9	60%	8,13	4,88	2,52
10	0%	15,09	0,00	3,00
11	5%	15,03	0,76	3,00
12	10%	15,01	1,51	3,00
13	15%	15,01	2,27	3,00

[a]% by weight of **1** respect of the fullerene mixture amount.

Table S4: Composition of fullerene mixtures upon extraction of as received fullerene mixture with variable amounts of receptor **1**

Entry	Ratio C_{60}:1	Ratio C_{70}:1	Ratio C_{84}:1	$[C_{60}]$ (M)	$[C_{70}]$ (M)	$[C_{84}]$ (M)	Mixture Composition[a] C_{60}	C_{70}	C_{84}	Recovery (%) C_{60}	C_{70}	C_{84}
1	1:0,00	1:0,00	1:0,00	$2,23x10^{-5}$	$7,20x10^{-6}$	$1,22x10^{-5}$	53	17	29	0,8	0,9	7
2	1:0,01	1:0,03	1:0,13	$2,28x10^{-5}$	$6,79x10^{-6}$	$1,25x10^{-5}$	54	16	30	0,8	0,8	7
3	1:0,02	1:0,08	1:0,40	$2,23x10^{-5}$	$7,03x10^{-6}$	$2,30x10^{-5}$	43	13	44	0,8	0,9	14
4	1:0,04	1:0,14	1:0,66	$2,18x10^{-5}$	$7,34x10^{-6}$	$5,49x10^{-5}$	26	9	65	0,7	0,9	31
5	1:0,08	1:0,28	1:1,32	$1,76x10^{-5}$	$1,02x10^{-5}$	$9,38x10^{-5}$	14	8	77	0,6	1,2	53
6	1:0,12	1:0,41	1:1,98	$2,19x10^{-5}$	$3,49x10^{-5}$	$1,15x10^{-4}$	13	20	67	0,7	4,2	66
7	1:0,16	1:0,55	1:2,64	$2,43x10^{-5}$	$5,82x10^{-5}$	$1,14x10^{-4}$	12	30	58	0,8	6,9	64
8	1:0,32	1:1,10	1:5,29	$3,47x10^{-5}$	$1,59x10^{-4}$	$1,20x10^{-4}$	11	51	38	1,2	19,1	69
9	1:0,47	1:1,65	1:7,93	$5,77x10^{-5}$	$2,35x10^{-4}$	$1,04x10^{-4}$	15	59	26	2,0	28,3	60
10	1:0,00	1:0,00	1:0,00	$2,32x10^{-5}$	$7,57x10^{-6}$	$1,75x10^{-5}$	48	16	36	0,5	0,6	7
11	1:0,04	1:0,14	1:0,66	$2,68x10^{-5}$	$8,97x10^{-6}$	$1,08x10^{-4}$	19	6	75	0,6	0,7	40
12	1:0,08	1:0,28	1:1,32	$2,81x10^{-5}$	$2,60x10^{-5}$	$1,72x10^{-4}$	12	11	76	0,6	2,0	64
13	1:0,12	1:0,41	1:1,98	$2,75x10^{-5}$	$5,98x10^{-5}$	$1,93x10^{-4}$	10	21	69	0,6	4,6	72

[a] % of each fullerene present in the mixture after the extraction.
[b]% of each fullerene with respect to the total amount of C_{60}, C_{70} and C_{84} respectively.

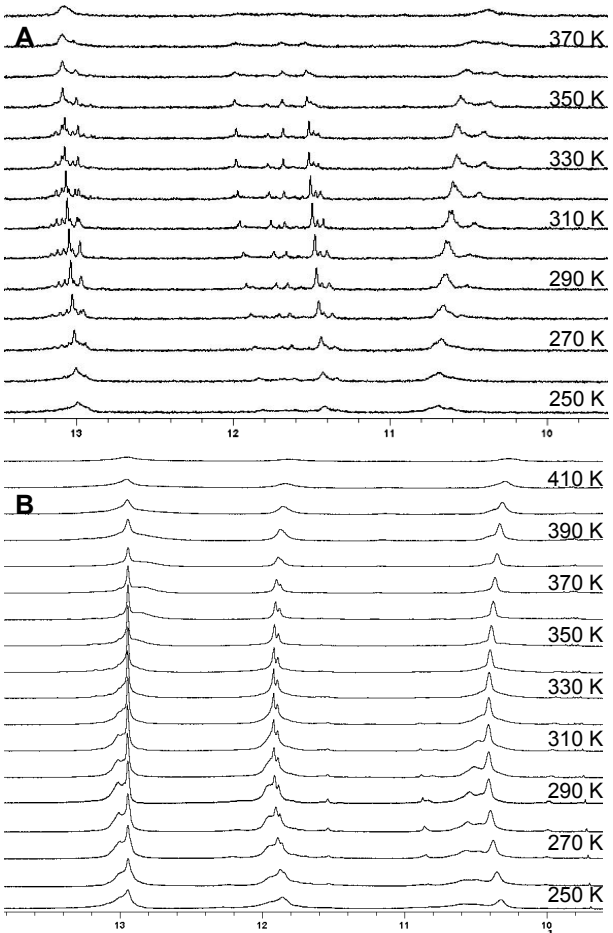

Figure S4: NH region (10-14 ppm) of a variable temperature ^{1}H-NMR experiment (TCE-d_2, 500 MHz) of: (A) **1** + 0.5 eq of C_{70}; (B) **1** + 0.5 eq of C_{84}.

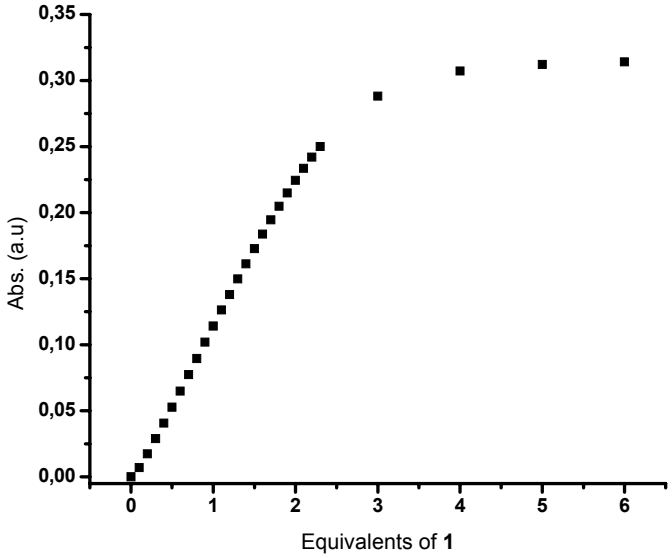

Figure S5. Binding isotherm for C_{84}@$\mathbf{1}_2$ in TCE (UV/vis).