Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

A Molecular Popeye: $Li^+@C_{60}$ and its Complexes with [n]Cycloparaphenylenes

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1. Experimental section

Chemicals: [n]CPPs were purchased from TCI (Belgium, HPLC grade), $[Li^+@C_{60}](PF_6)^-$ from Idea International Co., Ltd (Japan, 001D04) and trifluoroacetic acid (TFA) from Merck (Germany, HPLC) grad. The solvents acetonitrile (ACN), dichloromethane (DCM), *o*-dichlorobenzene (*o*-DCB) and toluene (tol) were purchased from VWR (Belgium, HPLC grade).

Sample preparation: Stock solutions of [n]CPPs were prepared in DCM (0.2 g l^{-1}), of C_{60} in tol (0.5 g l^{-1}) and of $[Li^+@C_{60}](PF_6)^-$ in *o*-DCB (0.5 g l^{-1}). The ESI experiments were performed with a solvent mixture of ACN/DCM/tol (3:2:1, v:v:v) to which a small amount of TFA was added. The analyte concentrations were 1 x 10^{-5} mol l^{-1} in case of [n]CPPs and C_{60} while the concentration of $[Li^+@C_{60}](PF_6)^-$ was 1 x 10^{-6} mol l^{-1}. The lower concentration of $[Li^+@C_{60}](PF_6)^-$ was chosen due to its ionic nature and, hence, to prevent saturation of our detector.

Instrumentation: The mass spectrometry experiments were performed on a quadrupole time-of-flight mass spectrometer (microToF-Q II, Bruker Daltonics, Bremen). For its ESI source, the analyte solutions were directly injected with a syringe pump at a flow rate of 180 µl h^{-1}. The temperature of the nitrogen counter flow was set to 180 °C and a capillary voltage of −4.5 kV was applied. Prior to each experiment, the instrument parameters were optimized to obtain good signal intensities. MS^2 experiments were carried out with N_2 as collision gas which was generated by a Parker LCMS64 nitrogen generator with a purity of 99.999% and a flow rate of 0.2 l min^{-1}.

The titration experiments were performed using a Nano ITC-low volume calorimeter from TA instruments. 25 injections were added from the computer-controlled 50 µl microsyringe into the corresponding host solution, each with a volume of 1.95 µl (unless otherwise indicated in the subtitle). The delay time was 200 s between each injection and the stirring rate was 350 rpm. All ITC experiments were performed at 25 °C and in triplicates. The respective initial injections were discarded in order to remove the effect of titrant diffusion across the syringe tip during the equilibration process. The heat change accompanying the addition of the guest into solvent (dilution and unspecific heat) were subtracted from the raw results by the software AFFINImeter. The concentrations used were 1 x 10^{-4} M for the compound in the injection syringe and 1 x 10^{-5} M for the compound in the titration cell. The experimental data were fitted to a theoretical titration

curve using the software AFFINimeter with ΔH (enthalpy change in kcal·mol^{-1}), K_a (association constant in M^{-1}) and n (stoichiometry), as adjustable parameters.
The thermodynamic parameters were calculated from Equation 1:

$$\Delta G = \Delta H - T\Delta S = -RT \cdot lnK_a \quad (1)$$

ΔG: change in free energy; ΔH: change in enthalpy; ΔS: change in entropy; T: absolute temperature; R: universal gas constant.

Breakdown graphs: Breakdown graphs are a plot of the Survival Yield (SY) against the applied collision energy. The SY is the ratio of precursor ions surviving the collision event at a given collision energy in relation to all ions observed. The collision energy is determined by dividing the laboratory energy (E_{lab}) by the degrees of freedom (DoF) of the hosting [n]CPP. This procedure of defining the collision energy is based on our previous results.[1] The number of DoF was calculated according to Equation 2:

$$DoF = (3 * n) - 6 \quad (2)$$

with n corresponding to the number of atoms of the [n]CPP.

All SY curves were recorded under multiple collision conditions and fitted with a sigmoid Boltzmann function. The collision energy, E_{50}, at which 50% of the parent ions have dissociated into their fragment ions is chosen as a relative measure of stability. The fragmentation energies obtained represent relative rather than absolute values with respect to the actual energy demand of the dissociation processes.

2. Additional experimental data

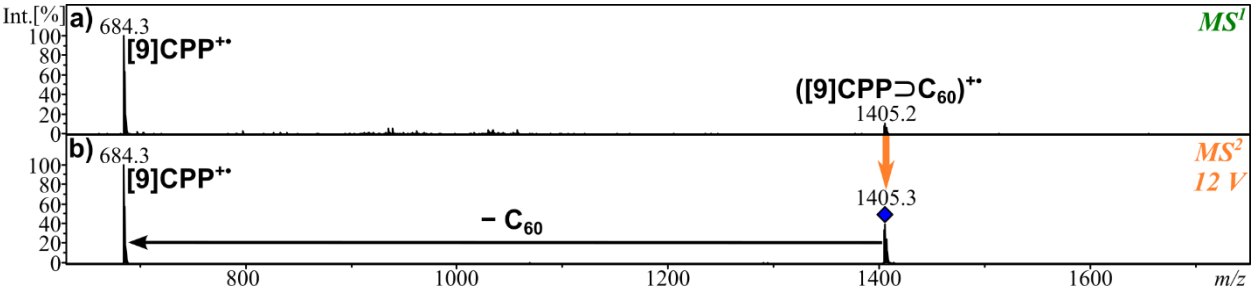


Figure S1. **a)** Positive-ion mode ESI MS^1 spectrum of a solution containing [9]CPP and C_{60}; **b)** MS^2 spectrum of $([9]CPP⊃C_{60})^{+\bullet}$.

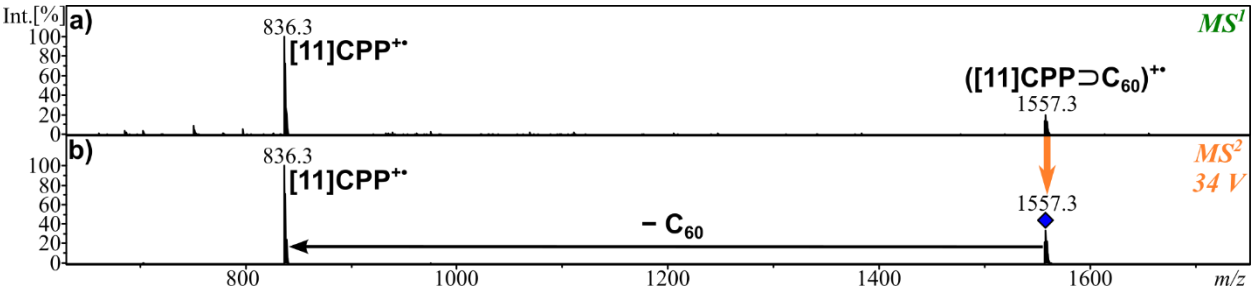


Figure S2. a) Positive-ion mode ESI MS^1 spectrum of a solution containing [11]CPP and C_{60}; **b)** MS^2 spectrum of $([11]CPP⊃C_{60})^{+\bullet}$.

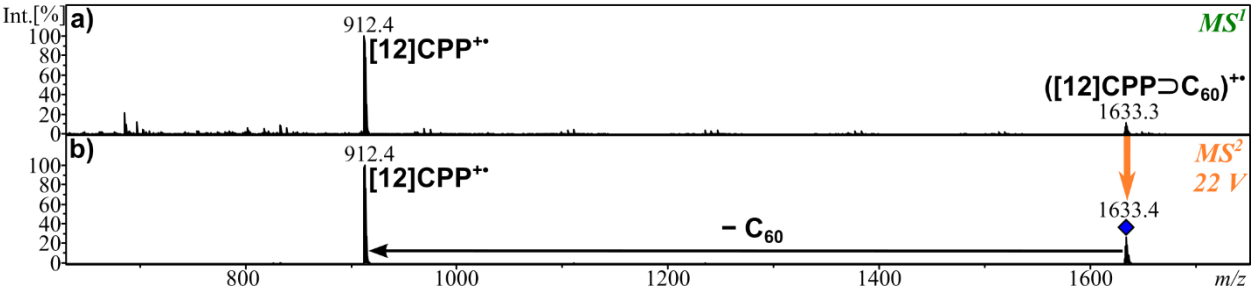


Figure S3. a) Positive-ion mode ESI MS^1 spectrum of a solution containing [12]CPP and C_{60}; **b)** MS^2 spectrum of $([12]CPP^{+\bullet}⊃C_{60})^{+\bullet}$.

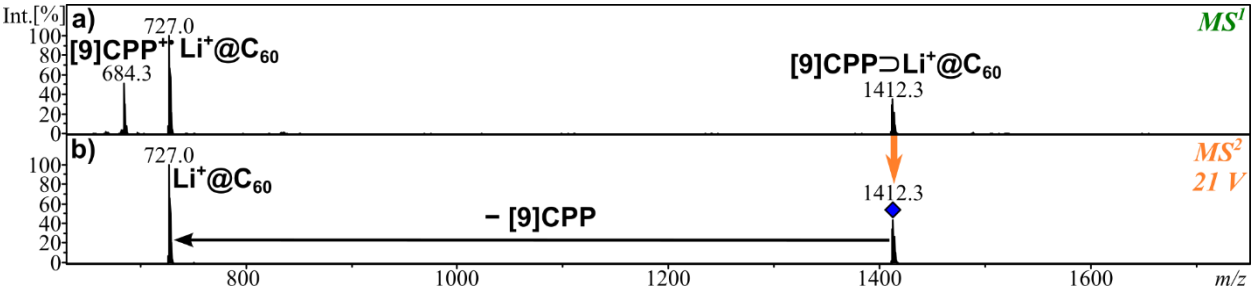


Figure S4. a) Positive-ion mode ESI MS^1 spectrum of a solution containing [9]CPP and $Li^+@C_{60}$; **b)** MS^2 spectrum of $[9]CPP⊃Li^+@C_{60}$.

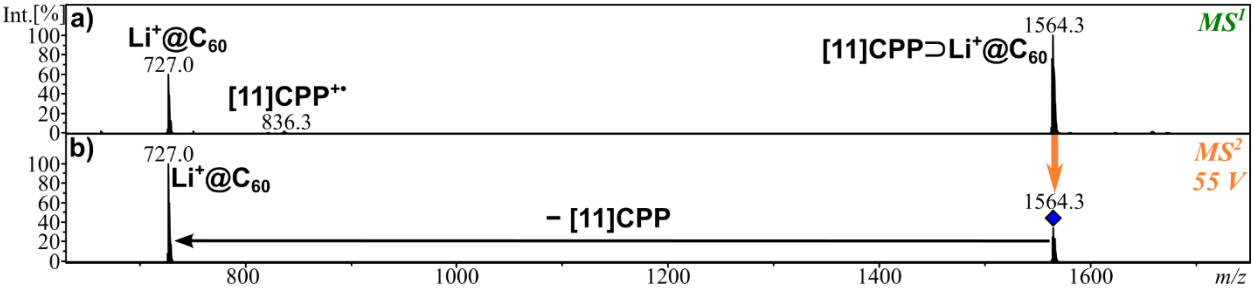


Figure S5. a) Positive-ion mode ESI MS^1 spectrum of a solution containing [11]CPP and $Li^+@C_{60}$; **b)** MS^2 spectrum of [11]CPP⊃$Li^+@C_{60}$.

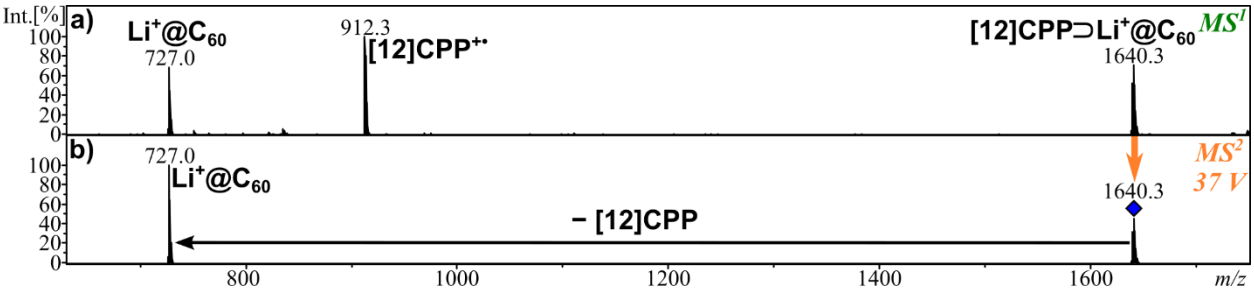


Figure S6. a) Positive-ion mode ESI MS^1 spectrum of a solution containing [12]CPP and $Li^+@C_{60}$; **b)** MS^2 spectrum of [12]CPP⊃$Li^+@C_{60}$.

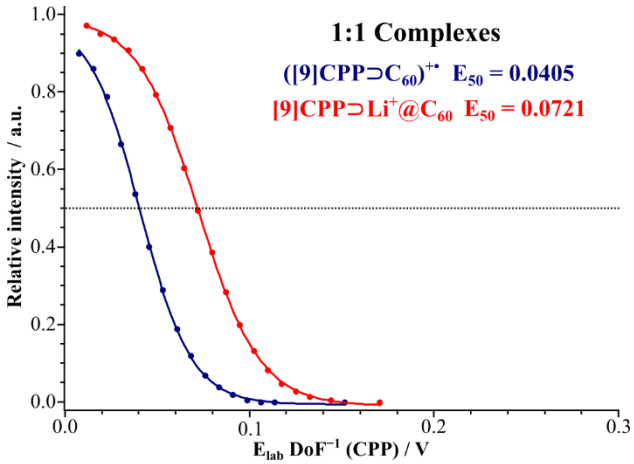


Figure S7. Energy-resolved collision-induced dissociation graphs of [9]CPP⊃$Li^+@C_{60}$ and $([9]CPP⊃C_{60})^{+\bullet}$.

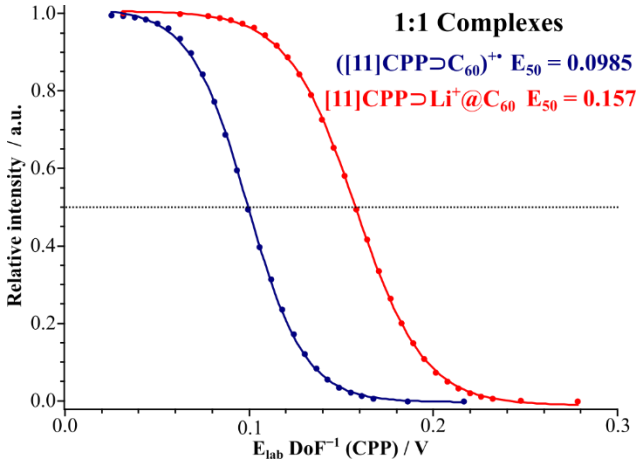


Figure S8. Energy-resolved collision-induced dissociation graphs of [11]CPP⊃Li^+@C_{60} and $([11]CPP⊃C_{60})^{+\bullet}$.

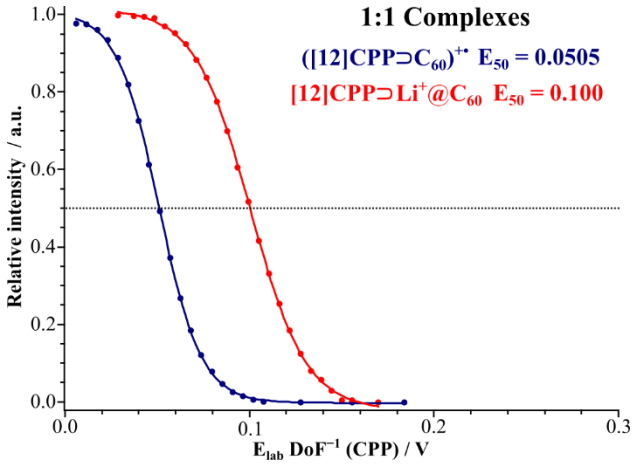
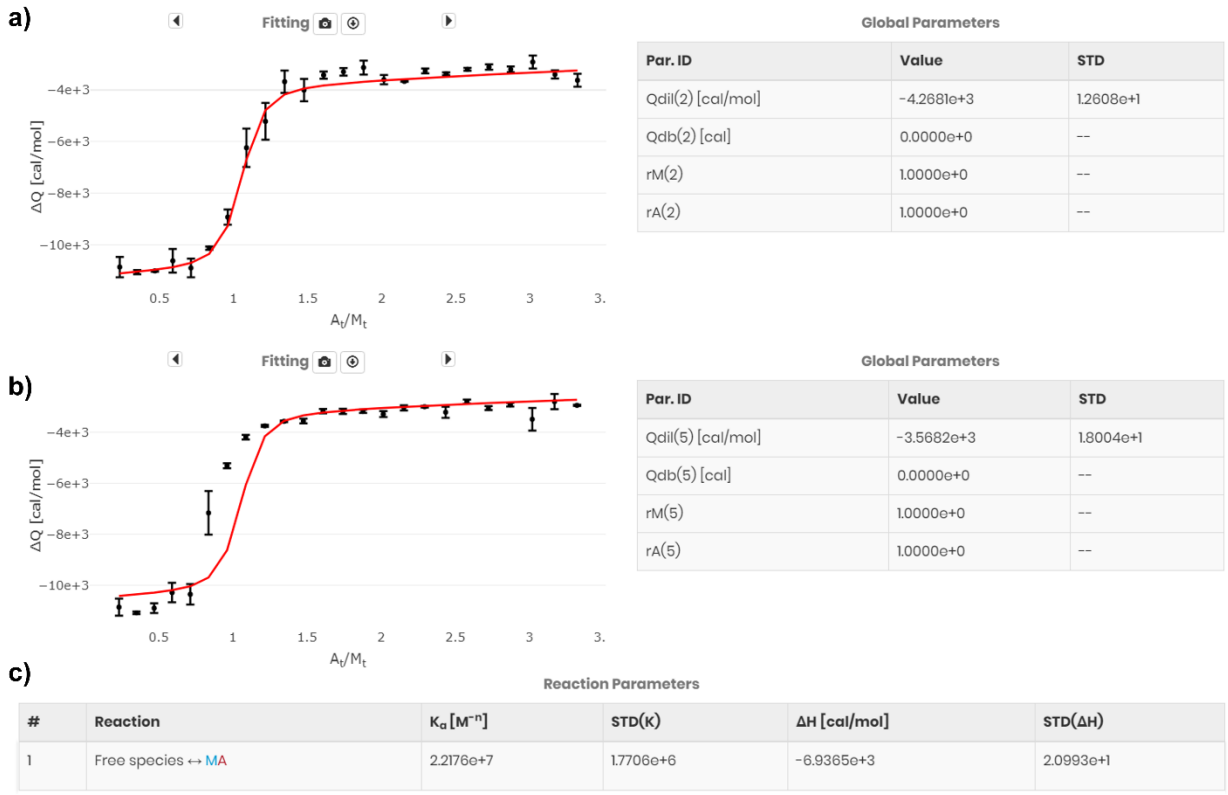


Figure S9. Energy-resolved collision-induced dissociation graphs of [12]CPP⊃Li^+@C_{60} and $([12]CPP⊃C_{60})^{+\bullet}$.



Global Parameters

Par. ID	Value	STD
Qdil(2) [cal/mol]	-4.2681e+3	1.2608e+1
Qdb(2) [cal]	0.0000e+0	--
rM(2)	1.0000e+0	--
rA(2)	1.0000e+0	--

Global Parameters

Par. ID	Value	STD
Qdil(5) [cal/mol]	-3.5682e+3	1.8004e+1
Qdb(5) [cal]	0.0000e+0	--
rM(5)	1.0000e+0	--
rA(5)	1.0000e+0	--

Reaction Parameters

#	Reaction	K_a [M^{-n}]	STD(K)	ΔH [cal/mol]	STD(ΔH)
1	Free species ↔ MA	2.2176e+7	1.7706e+6	-6.9365e+3	2.0993e+1

Figure S10. a, b) Representative ITC data of the global analysis of the triple titration of $Li^+@C_{60}$ into [10]CPP **(a)** together with the triple titration of [10]CPP into $Li^+@C_{60}$ **(b)** in *o*-DCB. Experimental data points (black points) and the fitting curve (red) using a [1:1] binding model from AFFINImeter software. **c)** Result of the global analysis providing one overall binding constant and one enthalpy value for all six experiments.

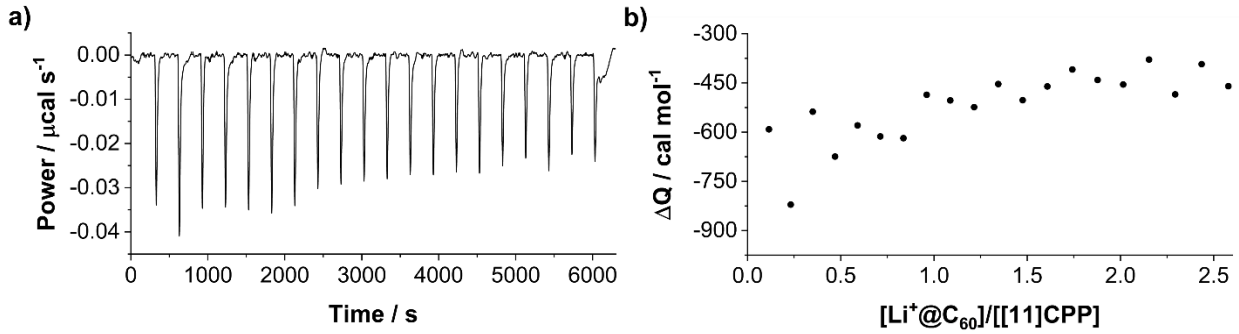


Figure S11. Titration of $Li^+@C_{60}$ (c = 8 x 10^{-4} M) into [11]CPP (c = 8 x 10^{-5} M) with 20 injections á 1.95 µl. **a)** ITC thermogram and **b)** experimental data points that cannot be fitted properly because of too less heats.

3. References

[1] M. Freiberger, M. B. Minameyer, I. Solymosi, S. Frühwald, M. Krug, Y. Xu, A. Hirsch, T. Clark, D. Guldi, M. von Delius, K. Amsharov, A. Görling, M. E. Pérez-Ojeda, T. Drewello, *Eur. J. Chem.*, in press, *n/a*.