Supporting Information

Fullerene Building Blocks with Tailor-Made Solubility and New Insights into Their Hierarchical Self-Assembly

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**Chemical Structures**

- **1**
  - Reaction with CBr$_4$ in Toluene, DBU, 72 h, RT

- **2 a-i**
  - Reaction with Toluene hv, 15 °C, 24 h

- **3 a-i**

**Chemical Compounds**

- **a-c** $\sim$-O(CH$_2$)$_n$CH$_3$ $n=1, 5, 17$
- **d** $\sim$-O
- **e** $\sim$-O
- **g-iBu** $\sim$-O
- **h-BOC** $\sim$-O
- **f** $\sim$-O
- **g** $\sim$-O
- **h** $\sim$-NH$_3\cdot$CF$_3$COO$^-$. 
- **i** $\sim$-O
S1. $^1$H/$^{13}$C/$^{19}$F NMR spectra

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) of isoxazolino fullerene 1.

Figure S2. $^{13}$C NMR (100 MHz, CDCl$_3$) of isoxazolino fullerene 1.
Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2a.

Figure S4. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2a.
Figure S5. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2b.

Figure S6. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2b.
**Figure S7.** $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2c.

**Figure S8.** $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2c.
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2d.

Figure S10. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2d.
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2e.

Figure S12. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2e.
Figure S13. $^1$H NMR spectrum of [5:1] fullerene 2f.

Figure S14. $^{13}$C NMR spectrum of [5:1] fullerene 2f.
Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene 2g-tBu.

Figure S16. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene 2g-tBu.
Figure S17. $^1$H NMR (400 MHz, CDCl$_3$) of [5:1] fullerene $2h_{BOC}$.

Figure S18. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:1] fullerene $2h_{BOC}$.}

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Figure S19. \(^1\)H NMR (400 MHz, C\(_6\)F\(_6\) : CDCl\(_3\) 1:1) of [5:1] fullerene 2i. The integrals of the CH\(_2\)CH\(_2\)CH\(_2\)CF\(_2\) are overestimated because of the perfluorinated impurity * which comes from the malonate synthesis. The mixture was used without further purification in the next step.

Figure S20. \(^1\)H NMR (300 MHz, CDCl\(_3\)) of impurity * obtained during malonate synthesis. Molecular weight calculated for C\(_{20}\)H\(_{18}\)F\(_{17}\)N\(_2\)O\(_2\) = 641,3414 found MS (MALDI-TOF, dctb): m/z = 641.0823 [M]\(^-\).
[5:0] pentakisadducts:

Figure S21. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3a.

Figure S22. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3a.
Figure S23. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3b.

Figure S24. $^{13}$C NMR (126.6 MHz, CDCl$_3$) of [5:0] fullerene 3b.
Figure S25. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3c.

Figure S26. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3c.
Figure S27. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3d.

Figure S28. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3d.
Figure S29. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3e.

Figure S30. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3e.
Figure S31. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3f.

Figure S32. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3f.
Figure S33. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3g-Bu.

Figure S34. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3g-Bu.
Figure S35. $^1$H NMR (400 MHz, CDCl$_3$) of [5:0] fullerene 3h$_{Boc}$.

Figure S36. $^{13}$C NMR (100 MHz, CDCl$_3$) of [5:0] fullerene 3h$_{Boc}$.
Figure S37. $^1$H NMR (400 MHz, C$_6$F$_6$/CDCl$_3$ 1:1) of [5:0] fullerene 3i.

Figure S38. $^{19}$F NMR (282 MHz, C$_6$D$_6$/C$_6$F$_6$ 1:1) of [5:0] fullerene 3i.
Figure S39. $^{13}$C NMR (100 MHz, C$_6$D$_6$/C$_6$F$_6$ 1:1) of [5:0] fullerene 3i.

Figure S40. $^1$H NMR (400 MHz, CD$_3$OD) of [5:0] fullerene 3g.
Figure S41. $^{13}$C NMR (100 MHz, CD$_3$OD) of [5:0] fullerene 3g.

Figure S42. $^1$H NMR (400 MHz, CD$_3$OD) of [5:0] fullerene 3h.
Figure S43. $^{13}$C NMR (100 MHz, CD$_3$OD) of [5:0] fullerene 3h.
S2. UV/vis and log $P$ measurements

Before the octanol-water partition experiments, the extinction coefficients $\varepsilon$ at $\lambda_{\text{max}} = 211$ nm were established using the Lambert Beer law (see equation below).

$$A = c \times l \times \varepsilon$$

The UV/vis spectra depicted in Figure S44 and S45 show the absorption bands at 211, 244 and 282 nm which are characteristic for fullerene pentakisadducts. For $3b$, $3c$, $3f$, $3g\text{-tBu}$ and $3h\text{-BOC}$, the extinction coefficient $\varepsilon$ was evaluated in octanol and for $3g$, $3h$, and $3f$ in phosphate buffered water at pH7. The perfluorinated compound $3i$ was dissolved in Freon 113 for the UV/vis measurements and Figure S46 shows its features.

![Figure S44. Absorption spectra of fullerene pentakisadducts in octanol.](image1)

![Figure S45. Absorption spectra of fullerene pentakisadducts in water.](image2)
Figure S46. Absorption spectrum of fullerene pentakisadduct 3i in Freon 113.

At least five different concentrations of the pentakisadducts were prepared and the absorption was measured by UV-vis. As an example, the linear fit for 3b is depicted in Figure S47. $\varepsilon$ was determined from the slope of the graph. The error of the fitting defined by $R^2$ lies in the range between 0.9783 - 0.9997.

Figure S47. Determination of the $\varepsilon$ of compound 3b.

The resulting values are summarized in Table S1 and are given for the maximum at $\lambda = 211$ nm or if a cut-off was observed at $\lambda = 282$ nm as indicated. For 3a and 3d the $\varepsilon$ was not determined due to solubility issues in octanol. The $\varepsilon$ is necessary to determine the concentration in the phases before and after equilibration for the log $P$ measurements.
| ε · 10^4(M⁻¹.cm⁻¹) at 211 nm | 3b | 3c | 3f | 3g_{abu} | 3h_{soc} | 3g | 3h | 3i |
|-----------------------------|----|----|----|-----------|-----------|----|----|----|
| octanol                    | 11.11 | 10.18 | 16.66 | 12.49 | 9.85 | 11.08 | 2.25 (282 nm) | - |
| water                      | - | - | 14.49 | - | - | 6.83 | 3.94 (282 nm) | |
| Freon 113                  | - | - | - | - | - | - | 8.45 (282 nm) | |

Table S1. Extinction coefficient ε of the fullerene pentakisadducts.

The octanol-water partition coefficient is a very useful method to establish the relative lipophilicity of a compound. It is defined by the following equation

\[ \log P = \log K_{ow} = \log \frac{c_o}{c_w} \]

This ratio is a measure of the difference in solubility of the compound in the octanol or water phase, respectively. UV/vis spectroscopy was used to determine the concentration of the compound in the octanol phase after equilibration. The octanol phase was previously saturated with water and the water phase was buffered at pH 7.0 for all neutral fullerenes (3a-f) using a sodium phosphate buffer (0.5 M). The log P of fullerenes 3g and 3h were evaluated under their ionized form due to solubility problems. Thus, phosphate buffered water at pH = 9.0 (0.5 M) for 3g and at pH = 4.4 (0.2 M) for 3h were used. The buffer solutions were purchased from Alfa Aesar. For the biphasic solutions, 2 mL of each phase were placed in a glass vial, the initial concentration was always prepared in 10^-4 mM range. The biphasic solutions were stirred with a Teflon stirring bar at high speed and at room temperature for 48 h. While co is the concentration in octanol, cw is defined as the concentration in water after the stirring. Additionally, the values of the dried samples were also taken into account. For that purpose, the octanol phase was dried with MgSO₄ anhydrous. Subsequently, the absorption can be measured and the log P for the dried sample can be re-evaluated. The difference between the log P and the log P dried, Δlog P is also listed in Table S2. All concentrations were evaluated from the octanol phase except for 3h due to its low solubility in octanol. In this case the log P was evaluated from the water phase using the ε in water (3.94 10^{-4} M⁻¹·cm⁻¹). However, for the log P dried, it has to be determined from the octanol phase, therefore its ε was evaluated using 1 % TFA as co-solvent. All experiments were conducted in duplicate and the average ± standard deviation was determined (Table S2). Fullerenes 3a, 3d and 3i were not evaluated due to their low solubility in both octanol and water.
|       | \(c_0\)    | \(c_W\)    | \(\log P\)  | \(\sigma \log P\) | \(\sigma \log P\) (dried) | \(\Delta \log P\) |
|-------|-----------|-----------|-------------|-----------------|---------------------------|-----------------|
| 3b    | 6.89 E-04 | 1.02 E-05 | 1.829726    | 1.94 ± 0.15     | 2.24 ± 0.76               | 0.30            |
|       | 6.93 E-04 | 6.23 E-06 | 2.046114    |                 |                           |                 |
| 3c    | 2.52 E-04 | 8.94 E-05 | 0.449442    | 0.46 ± 0.01     | 1.24                      | 0.78            |
|       | 2.54 E-04 | 8.72 E-05 | 0.464292    |                 |                           |                 |
| 3f    | 3.21 E-04 | 6.99 E-05 | 0.662332    | 0.62 ± 0.07     | 1.07                      | 0.45            |
|       | 3.08 E-04 | 8.32 E-05 | 0.568144    |                 |                           |                 |
| 3g_{-tBu} | 5.24 E-04 | 4.51 E-05 | 1.065095    | 1.06 ± 0.001    | 0.94 ± 0.13               | -0.12           |
|       | 5.23 E-04 | 4.52 E-05 | 1.063538    |                 |                           |                 |
| 3h_{BOC} | 4.25 E-04 | 1.01 E-04 | 0.622963    | 0.63 ± 0.01     | 0.65                      | 0.02            |
|       | 4.27 E-04 | 9.94 E-05 | 0.633398    |                 |                           |                 |
| 3g (pH 9.0) | 1.40 E-04 | 2.47 E-04 | -0.247324   | -0.32 ± 0.10    | -0.62                     | 0.30            |
|       | 1.12 E-04 | 2.75 E-04 | -0.391169   |                 |                           |                 |
| 3h (pH 4.4) | 5.27 E-05 | 6.46 E-04 | -1.089030   | -1.06 ± 0.03    | -1.01                     | 0.05            |
|       | 6.11 E-05 | 6.55 E-04 | -1.030228   |                 |                           |                 |

Table S2. Octanol-water partition coefficient \(\log P\) calculations for fullerene pentakisadducts.

**Figure S48.** Drying process with MgSO\(_4\)

**Figure S49.** \(\log P\) experiment for compound 3f showing tendency towards the octanol phase despite its water solubility (positive \(\log P\) value) after 48 h equilibration time.
Figure S50. Solubility evaluation for the ionisable fullerenes at different pH using sodium phosphate buffer. As expected, fullerene 3g is only soluble under basic conditions (pH = 9.0) while fullerene 3h is soluble under acidic ones (pH = 4.4).
S3. Contact angle measurements

Series 5 mg/mL and 20 mg/mL spin coated on glass wafer at 2500 rpm /acceleration 500/ 10 s
Contact angle measured on 3µL H₂O drop

| mg/ml | 3i | 3c | 3d | 3b | 3a | 3h-BOC | 3g-tBu | 3e | 3g | 3h | 3e | TEG |
|-------|----|----|----|----|----|--------|--------|----|----|----|----|-----|
| 5     | 118.72 ±9.46 | 112.63 ±2.26 | 111.45 ±3.13 | 106.32 ±2.80 | 88.98 ±2.37 | 92.60 ±1.04 | 87.60 ±2.16 | 74.88 ±3.29 | 75.17 ±1.21 | 55.72 ±0.99 | 47.03 ±9.87 |
| 20    | 119.45 ±1.57 | 140.60 ±6.29 | 92.16 ±5.46 | 108.05 ±1.80 | 94.48 ±3.98 | 110.43 ±3.84 | 105.27 ±4.92 | 77.34 ±2.18 | 82.95 ±1.45 | 11.23 ±0.88 | 32.87 ±4.67 |

Figure S51. Static contact angle measurements for two different concentrations (5 and 20 mg/mL) to evaluate the influence of the higher thickness in the observed angle.
Figure S52. Dynamic scanning calorimetry of compound 3c (EXO, up). Up: First and second heating at 10 C°/min. Down: cooling at -10 C°/min.
Differential scanning calorimetry reflects the endothermic melting transition at 39.05 °C, which is convoluted by two transitions for the first heating as can be observed in Figure S53 at slower scan rate. This two probably correspond to the two possible arrangements in solid state before melting to the fluidlike state.[1] No additional events were found outside this temperature range.
Figure S54. Cryo-TEM micrograph of octanol phase from blank experiment (stirred biphasic system octanol/water)
Figure S55. Cryo-TEM micrograph of compound 3c in octanol phase originary from partition coefficient experiment. Scale bar 200 nm.

References

[1] M. Hetzer, T. Gutberlet, M. F. Brown, X. Camps, O. Vostrowsky, H. Schönberger, A. Hirsch, T. M. Bayerl, *The Journal of Physical Chemistry A* **1999**, *103*, 637-642.