Supporting Information

Hexakis-Adducts of [60]Fullerene as Molecular Scaffolds of Polynuclear Spin-Crossover Molecules

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1. General methods for synthesis and characterization

Reagents and solvents were purchased as reagent grade and used without further purification. Compounds P1,\(^1\) bppCOOH,\(^2\) bppCOOEt (L1),\(^2\) bppCH\(_2\)OH (L3)\(^3\) and L6\(^4\) were prepared according to previously reported procedures. Purification was carried out by column chromatography using silica gel 60 (230–400 mesh, 0.040–0.063 mm) purchased from E. Merck or by Sephadex LH20 (GE Healthcare, Barcelona, Spain) gel filtration. Thin layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F\(_{254}\) purchased from E. Merck, visualization by UV light. IR spectra (cm\(^{-1}\)) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 or AC 500 with solvent peaks as reference. \(^1\)H and \(^13\)C NMR spectra were obtained for solutions in CDCl\(_3\), CD\(_3\)OD and DMSO-\(d_6\). All the assignments were confirmed by one- and two-dimensional NMR experiments (COSY, HSQC and DEPT). Mass spectra were registered on a Bruker BIFLEXTM matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometer using 2-[(E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. Electrospray ionization (ESI) mass spectra were recorded with an Esquire 6000 ESI-Ion Trap from Bruker Daltonics using CH\(_2\)Cl\(_2\)/MeOH as solvent system. UV-vis absorption spectra were recorded on a Varian Cary 100 Bio spectrometer and emission spectra were recorded on a PTI spectrofluorometer. Luminescence decays were measured using a Compact fluorescence lifetime spectrometer C11367, Quantaurus-Tau. The photoluminescence (PL) lifetime measurement software U11487 was used to register the data. The PL decays were fitted to a biexponential function.
2. Synthesis and characterization of 1, 2, 3 and 4

**Synthesis of compound 1.**

Scheme S1. Schematic representation of the synthesis of 1

To a solution of P1 (140 mg, 65.10 μmol), ligand bppCOOH (299 mg, 1.17 mmol) and DPTS (115 mg, 0.39 mmol) in a dry mixture of CH₂Cl₂/DMF (6 mL, 3:1) under Ar atmosphere, and DCC (244 mg, 1.17 mmol) in dry CH₂Cl₂ (1.5 mL) were added. The reaction mixture was stirred at 40 °C overnight. Once the reaction was complete, the dicyclohexylurea was filtered off in a fritted glass filter and washed with CH₂Cl₂. The crude product was purified by size-exclusion chromatography (Sephadex LH-20, MeOH/CH₂Cl₂ 1:1), to give 1 (331 mg, quant.) as an orange-red amorphous solid. IR (neat): 3115, 2960, 1731, 1463, 1397, 1239, 1042 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ/ppm: 8.40 (m, 24H, H-Aryl), 8.19 (m, 24H, H-Aryl), 7.70 (m, 24H, H-Aryl), 6.41 (m, 24H, H-Aryl), 4.37 (m, 48H, OCH₂CH₂CH₂CH₂O), 1.89 (m, 48H, OCH₂CH₂CH₂CH₂O); ¹³C NMR (125.8 MHz, CDCl₃) δ/ppm: 163.7 (CO), 163.6 (CO), 150.5 (C₁₉Ar-N), 145.9 (C₁₉Ar-CO), 143.0 (C₁₉Ar-CO), 142.7 (CH-Aryl), 141.2 (C₁₉Ar-CO), 127.0 (CH-Aryl), 108.8 (CH-Aryl), 108.3 (CH-Aryl), 69.2 (C₁₉Ar-CO), 66.4, 65.4 (OCH₂CH₂CH₂CH₂O), 45.4 (C₄bridge), 25.2, 25.1 (OCH₂CH₂CH₂CH₂O); MALDI-TOF (DCTB): m/z calcd for C₂₇₀H₁₉₂N₆₀O₄₈: 5044.9; found: 5044.1 [M⁺], 5067.2 [M+Na⁺], 5083.2 [M+K⁺].
Figure S1. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 1

Figure S2. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound 1
**Figure S3.** MALDI-TOF spectrum of compound 1

**Synthesis of compound 2.**

**Scheme S2.** Schematic representation of the synthesis of 2
To a solution of bppCH₂OH (L₃) (300 mg, 1.24 mmol) and succinic anhydride (149 mg, 1.49 mmol) in dry CH₂Cl₂ (8 mL), DMAP (152 mg, 1.24 mmol) was added. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum and Et₂O (10 mL) was added. The resulting solution was washed with 5% Na₂CO₃ (20 mL). The aqueous layer was brought to pH 4 by adding 1 M HCl (20 mL). The resulting aqueous solution was extracted three times with Et₂O. The organic layers were washed with brine, dried over MgSO₄, filtered and reduced under vacuum, to give compound L₄ (360 mg, 86%) as a white amorphous solid. ¹H NMR (300 MHz, DMSO-d₆) δ/ppm: 12.27 (s, 1H, COOH), 8.95 (d, J = 2.6 Hz, 2H, H-ArpzyI), 7.88 (m, 2H, H-ArpzyI), 7.80 (s, 2H, H-Arpy), 6.64 (dd, J = 2.6, 1.6 Hz, 2H, H-ArpzyI), 5.32 (s, 2H, CH₂,Bn), 2.67 (m, 2H, CH₂,succ.), 2.55 (dd, J = 6.9, 2.3 Hz, 2H, CH₂,succ.); ¹³C NMR (75 MHz, DMSO-d₆) δ/ppm: 173.3 (CO), 172.0 (CO), 152.2 (CipsoAr-CH₂,Bn), 149.8 (CipsoAr-N), 142.8 (CH-ArpzyI), 128.2 (CH-ArpyL), 108.5 (CH-ArpyL), 106.8 (CH-Arpy), 63.9 (CH₂,Bn), 28.6 (CH₂,succ.); ESI-HRMS: m/z calcd for C₁₈H₁₇N₃O₄Na [M+Na]⁺: 364.3168; found: 364.3172.

Figure S4. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of compound L₄
Figure S5. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$) of compound L4

Compound 2.
To a solution of P1 (61 mg, 27.85 μmol), ligand L3 (170 mg, 0.50 mmol) and DPTS (49 mg, 0.17 mmol) in a dry mixture of CH₂Cl₂/DMF (3 mL, 2:1) under Ar atmosphere, DCC (105 mg, 0.50 mmol) in dry CH₂Cl₂ (1 mL) was added. The reaction mixture was stirred at 40 °C overnight. Once the reaction was complete, the dicyclohexylurea was filtered off in a fritted glass filter and washed with CH₂Cl₂. The crude product was purified by size-exclusion chromatography (Sephadex LH-20, MeOH/CH₂Cl₂ 1:1), to give 2 (170 mg, quant.) as an orange-red amorphous solid. IR (neat): 3132, 2959, 2926, 1733, 1463, 1394, 1206, 1154, 1040 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ/ppm: 8.50 (m, 24H, H-Arpyzl), 7.81–7.66 (m, 48H, H-Arpy, H-Arpyzl), 6.45 (m, 24H, H-Arpyz), 5.20 (s, 24H, CH₂,Bn), 4.27 (m, 24H, OCH₂CH₂), 4.10 (m, 24H, OCH₂CH₂), 2.75 (m, 24H, CH₂,succ.), 2.66 (m, 24H, CH₂,succ.), 1.78–1.65 (m, 48H, OCH₂CH₂CH₂CH₂O); ¹³C NMR (125.8 MHz, CDCl₃) δ/ppm: 172.0 (CO), 171.7 (CO), 163.6 (CO), 151.0 (Cipso-Ar-CH₂,Bn), 150.1 (Cipso-Ar-N), 145.7 (Csp₂,fullerene), 142.3 (CH-Arpyz), 141.0 (Csp₂,fullerene), 127.0 (CH-Arpyz), 108.0 (CH-Arpy), 107.1 (CH-Arpyz), 69.0 (Csp₃,fullerene), 66.4 (OCH₂CH₂), 64.3 (CH₂,Bn), 63.9 (OCH₂CH₂), 45.3 (Cq,bridge), 28.8 (CH₂,succ.), 25.0 (OCH₂CH₂CH₂CH₂O); MALDI-TOF (DCTB): m/z calcd for C₃₁₈H₂₆₄N₆₀O₇₂: 6073.9; found: A high level of occurring fragmentation avoided the observation of the expected molecular ion peak.

Figure S6. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 2
Figure S7. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound 2

Synthesis of compound 3.

Scheme S3. Schematic representation of the synthesis of 3
MeppCOOH (L5)

In an Ar atmosphere, NaH (274 mg, 11.4 mmol) was suspended in dry dyglime (8 mL), then 4-methylpyrazole (615 µL, 7.4 mmol) was added dropwise to form a white suspension that turned into a yellowish solution upon heating to 80 °C for 90 minutes. 2,6-Dibromoisonicotinic acid (540 mg, 1.92 mmol) was then added and the suspension was heated to 120 °C for 3 days. The solvent was evaporated leaving a very small volume left and water (50 mL) was added. This suspension was acidified with HCl (1 M) to pH 2.75. A white product was formed, which was filtered, washed and dried to the air to give compound L5 (500 mg, 93%). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$/ppm: 8.74 (d, $J = 2.6$ Hz, 2H, H-Arpyzl), 8.07 (m, 2H, H-Arpyzd), 7.73 (s, 2H, H-Arpy), 2.15 (s, 6H, CH$_2$succ.). $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$/ppm: 165 (CO), 150.8 (CipsoAr-CO), 144.6 (CipsoAr-N), 144.4 (CH-Arpyzd), 126.8 (CH-Arpyzd), 119.26 (C-Arpyzd), 107.6 (CH-Arpy), 9.22 (CH$_3$). ESI-HRMS: $m/z$ calcd for C$_{14}$H$_{13}$N$_5$O$_2$Na [M+Na]+: 306.0889; found: 306.0955

Figure S8. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$) of L5
Figure S9. $^{13}$C NMR spectrum (500 MHz, DMSO-$d_6$) of L5

Compound 3.

To a solution of P1 (118 mg, 53.72 μmol), L5 (274 mg, 0.97 mmol) and DPTS (95 mg, 0.32 mmol) in a dry mixture of CH$_2$Cl$_2$/DMF (6 mL, 3:1) under Ar atmosphere, DCC (202 mg, 0.97 mmol) in dry CH$_2$Cl$_2$ (1.5 mL) was added. The reaction mixture was stirred at 40 ºC overnight. Once the reaction was complete, the dicyclohexylurea was filtered off.
in a fritted glass filter and washed with CH$_2$Cl$_2$. The crude product was purified by size-exclusion chromatography (Sephadex LH-20, MeOH/CH$_2$Cl$_2$ 1:1), to give 3 (289 mg, quant.) as an orange-red amorphous solid. IR (neat): 2959, 2925, 1730, 1452, 1214 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ppm: 8.13 (m, 24H, H-Ar$_{pyz}$), 8.06 (m, 24H, H-Ar$_{py}$), 7.49 (m, 24H, H-Ar$_{pyz}$), 4.37, 4.33 (2m, 48H, OCH$_2$CH$_2$CH$_2$CH$_2$O), 2.10 (s, 72H, CH$_3$), 1.88 (m, 48H, OCH$_2$CH$_2$CH$_2$CH$_2$O); $^{13}$CN MR (125.8 MHz, CDCl$_3$) $\delta$ppm: 163.9 (CO), 163.8 (CO), 150.5 (C$_{ipso}$Ar-N), 145.9 (C$_{sp2,fullerene}$), 143.6 (CH-Ar$_{pyz}$), 142.6 (C$_{ipso}$Ar-CO), 141.2 (C$_{sp2,fullerene}$), 125.3 (CH-Ar$_{pyz}$), 118.8 (C-Ar$_{pyz}$), 107.9 (CH-Ar$_{py}$), 69.2 (C$_{sp3,fullerene}$), 66.5, 65.3 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 45.4 (C$_{q,bridge}$), 25.2, 25.1 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 9.0 (CH$_3$); MALDI-TOF: m/z calcd for C$_{294}$H$_{240}$N$_{60}$O$_{48}$: 5380.5; found: 5380.7 [M]$^+$, 5220.8 [M-2(methylpyrazol)+2H]$^+$.

Figure S10. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 3.
Figure S11. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound 3

Figure S12. MALDI-TOF spectrum of compound 3
Synthesis of compound 4.

Scheme S4. Schematic representation of the synthesis of 4

Compound P2.

DBU (633 μL, 4.23 mmol) (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) was added to a solution of fullerene C_{60} (2.44 g, 3.39 mmol), malonate L6 (725 mg, 1.69 mmol) and I₂ (1.5 g, 5.93 mmol) in dry toluene (300 mL) at 0 °C under Ar atmosphere. The resulting solution was stirred at 0 °C for 4 h. After this time, the organic layer was washed with saturated Na₂S₂O₃ (40 mL), dried over anhydrous MgSO₄, filtered and concentrated. The resulting crude was purified by silica gel chromatography column (hexane/CH₂Cl₂, 1:3), furnishing monoadduct P2 (1.5 g, 77%) as a brown amorphous solid. IR (neat): 2954,
2924, 2857, 1745, 1235, 737 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta/\text{ppm}\): 7.34 (m, 8H, H-Ar), 7.28 (m, 2H, H-Ar), 4.54–4.49 (m, 8H, CH\(_2\)Bn, OCH\(_2\)CH\(_2\)), 3.53 (t, 4H, \(J = 6.2\) Hz, CH\(_2\)CH\(_2\)OBn), 1.95 (m, 4H, OCH\(_2\)CH\(_2\)), 1.79 (m, 4H, CH\(_2\)CH\(_2\)OBn); \(^{13}\)C NMR (125.8 MHz, CDCl\(_3\)) \(\delta/\text{ppm}\): 163.5 (CO), 145.3, 145.2, 145.2, 145.1, 144.8, 144.7, 144.6, 144.56, 143.8, 143.1, 143.0, 142.9, 142.2, 141.9, 140.9, 139.0 (C\(_{\text{sp2, fullerene}}\)), 138.4 (C\(_{\text{ipso-Ar}}\)), 128.4, 127.6, 127.5 (C-Ar), 72.9 (CH\(_2\)Bn), 71.6 (C\(_{\text{sp3, fullerene}}\)), 69.5 (CH\(_2\)CH\(_2\)OBn), 67.2 (OCH\(_2\)CH\(_2\)), 52.2 (C\(_q, \text{bridge}\)), 26.2 (CH\(_2\)CH\(_2\)OBn) 25.6 (OCH\(_2\)CH\(_2\)); HRMS (MALDI-TOF): \(m/z\) calcd for C\(_{85}\)H\(_{30}\)O\(_6\) [M]: 1146.2042; found: 1146.2077.

**Figure S13.** \(^1\)H NMR spectrum (500 MHz, CDCl\(_3\)) of compound P2
Figure S14. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound P2
A solution of P2 (1.3 g, 1.13 mmol) in a mixture of CH$_2$Cl$_2$/MeOH (72 mL, 3:1) was hydrogenated under atmospheric pressure at room temperature overnight using Pd-C (10%) as catalyst. Then, the solution was filtered through celite, and the catalyst was washed with CH$_2$Cl$_2$/MeOH. The filtered solution was concentrated, furnishing pure P3 (1.03 g, 94%) as a brown amorphous solid. IR (neat): 3308, 2922, 1741, 1234, 753 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$ + CD$_3$OD) δ/ppm: 4.43 (t, 4H, $J = 6.6$ Hz, OCH$_2$CH$_2$), 3.58
(t, 4H, J = 6.5 Hz, CH₂CH₂OH), 1.84 (m, 4H, OCH₂CH₂), 1.64 (m, 4H, CH₂CH₂OH); 
¹³C NMR (125.8 MHz, CDCl₃) δ/ppm: 163.8 (CO), 145.4, 145.4, 145.3, 145.3, 145.1, 
144.9, 144.8, 144.0, 143.3, 143.2, 143.1, 142.4, 142.0, 141.1, 139.2 (C$_{\text{sp2, fullerene}}$), 71.7 
(C$_{\text{sp3, fullerene}}$), 67.4 (OCH₂CH₂), 62.4 (CH₂CH₂OH), 52.3 (C$_{\text{q, bridge}}$), 29.2 (CH₂CH₂OH), 
25.3 (OCH₂CH₂); HRMS (MALDI-TOF): m/z calcd for C$_{71}$H$_{18}$O$_{6}$ [M]$^+$: 966.1103; found: 
966.1078.

**Figure S16.** $^1$H NMR spectrum (500 MHz, CDCl₃) of compound P₃
Figure S17. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound P3
Figure S18. MALDI-TOF spectrum of compound P3

Compound 4.

To a solution of P3 (900 mg, 0.93 mmol), ligand L1 (713 mg, 2.79 mmol) and DPTS (274 mg, 0.93 mmol) in a dry mixture of CH$_2$Cl$_2$/DMF (48 mL, 3:1) under Ar atmosphere, DCC (582 mg, 2.79 mmol) in dry CH$_2$Cl$_2$ (12 mL) was added. The reaction mixture was stirred at 40 °C overnight. Once the reaction was complete, the dicyclohexylurea was
filtered off in a fritted glass filter and washed with CH$_2$Cl$_2$. The crude product was purified by silica gel chromatography column (toluene/acetone, 20:1), to give 4 (1.14 g, 85%) as a brown amorphous solid. IR (neat): 2959, 2926, 2855, 1732, 1462, 1237, 763 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$/ppm: 8.52 (dd, 4H, $J = 2.7, 0.7$ Hz, H-Ar$_{pyz}$), 8.33 (s, 4H, H-Ar$_{py}$), 7.77 (d, 4H, $J = 2.2$ Hz, H-Ar$_{pyz}$), 6.50 (dd, 4H, $J = 2.6, 1.6$ Hz, H-Ar$_{pyz}$), 4.61 (m, 4H, OCH$_2$CH$_2$), 4.48 (m, 4H, OCH$_2$CH$_2$), 2.03 (m, 8H, OCH$_2$CH$_2$CH$_2$CH$_2$O); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$/ppm: 163.9 (CO), 163.6 (CO), 150.8 (C$_{ipso}$Ar-N), 145.2, 145.2, 145.2, 144.9, 144.7, 144.6, 144.6, 143.8 (C$_{sp2,fullerene}$), 143.2 (C$_{ipso}$Ar-CO), 143.0, 143.0, 142.9 (C$_{sp2,fullerene}$), 142.9 (CH-Ar$_{pyz}$), 142.2, 141.8, 140.9, 139.0 (C$_{sp2,fullerene}$), 127.3 (CH-Ar$_{pyz}$), 109.1(CH-Ar$_{py}$), 108.5 (CH-Ar$_{pyz}$), 71.5 (C$_{sp3,fullerene}$), 66.8, 65.4 (OCH$_2$CH$_2$CH$_2$O), 52.1 (C$_{q,bridge}$), 25.5, 25.4 (OCH$_2$CH$_2$CH$_2$O); HRMS (MALDI-TOF): $m$/z calcd for C$_{96}$H$_{33}$N$_9$O$_8$ [M]$^+$: 1440.3750; found: 1440.2426.

Figure S19. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 4
Figure S20. $^{13}$C NMR spectrum (125.8 MHz, CDCl$_3$) of compound 4

Figure S21. MALDI-TOF spectrum of compound 4
3. Studies in solution

3.1 UV-vis spectra of 1, 2 and model ligands with Fe$^{2+}$.

**Figure S22.** UV-vis spectra of a titration of a 5 × 10$^{-5}$ M solution of model ligands a) bppCOOEt and b) bppCH$_2$OH in CH$_2$Cl$_2$ with Fe(BF$_4$)$_2$. 
Figure S23. UV-vis spectra of $7.5 \times 10^{-6}$ M solutions of a) 1 and b) 2 in CH$_2$Cl$_2$ with six equivalents of Fe(BF$_4$)$_2$ (red line) or Fe(ClO$_4$)$_2$ (black line).
3.2 Fluorescence titrations of 1, 2 and model ligands with Fe$^{2+}$.

**Figure S24.** Fluorescence spectra of a titration of $5 \times 10^{-5}$ M solution of a) bppCOOEt and b) bppCH$_2$OH in CH$_2$Cl$_2$ with Fe(BF$_4$)$_2$. 
Hexa-adduct 1 and bppCOOEt exhibit a very short excited-state lifetime indicating that they correspond to ligand fluorescence. The lifetime of 1 (τ = 0.15 ns) decreases one order of magnitude with respect to bppCOOEt ligand (τ = 2.36 ns). After addition of Fe$^{2+}$ equivalents, longer-lived components appear to have a greater contribution to the luminescence decay of 1 (τ ~ 4 ns (6 %) with 6 eqs) and bppCOOEt (τ ~ 5 ns (15 %) with 2 eqs).

Figure S25. Emission lifetime measurements of 1 and model ligand bppCOOEt.
Figure S26. Emission intensity values of $5 \times 10^{-6}$ M solutions after correcting inner filter effects of a) 1 and b) 2 upon addition of Fe(ClO$_4$)$_2$. 
Figure S27. Fluorescence spectra of a $5 \times 10^{-6}$ M solution of 1 (black line) after addition of 6 equivalents of Fe(ClO$_4$)$_2$ (red line) and 16 equivalents of 1,10-phenanthroline (phen) (green line).
3.3 Absorption and fluorescence titration of methylated derivative 3 with Fe(ClO$_4$)$_2$

UV-vis and fluorimetric titrations of the methylated derivative 3 presented a similar behavior to that of 1 with a MLCT band in the UV-vis spectrum at 469 nm and an emission of the ligand centered at 390 nm, which was completely quenched after addition of 6 equivalents of Fe$^{2+}$. This is consistent with a LS state of the metal complexes of this ligand. The same trend was observed for the unsubstituted bpp ligand.\textsuperscript{4}

**Figure S28.** a) UV-vis and b) fluorescence spectra of a titration of a $7.5 \times 10^{-6}$ M solution of 3 in CH$_2$Cl$_2$ with Fe(BF$_4$)$_2$. Black (0 eq.), red (1 eq.), dark green (2 eq.), blue (3 eq.), clear green (4 eq.), pink (5 eq.) and orange (6 eq.). Excitation wavelength was 320 nm.
3.4 UV-vis absorption and fluorescence titrations of 4.

Figure S29. a) UV-vis and b) fluorescence spectra of a $1.5 \times 10^{-5}$ M solution of 4 after addition of up to 1.5 equivalents of Fe(ClO$_4$)$_2$. Black (0 eq.), red (0.25 eq.), dark green (0.5 eq.), blue (0.75 eq.), clear green (1 eq.) and pink (1.5 eq.). Excitation wavelength was 285 nm.
Figure S30. a) UV-vis and b) fluorescence spectra of a $4.5 \times 10^{-5}$ M solution of 4 after addition of up to 0.75 equivalents of Fe(ClO$_4$)$_2$ Black (0 eq.), red (0.125 eq.), dark green (0.25 eq.), blue (0.375 eq.), clear green (0.5 eq.), pink (0.675 eq.) and orange (0.75 eq.). Excitation wavelength was 285 nm.
3.5 Excitation and absorption spectra of 1, 2 and 4

Figure S31. Excitation and absorption spectra of $7.5 \times 10^{-6}$ M solutions of a) 1, b) 2 and c) 4 in CH$_2$Cl$_2$. 
3.6 Temperature dependence of UV-vis absorption spectra of 2

**Figure S32.** UV-vis spectra of a $7.5 \times 10^{-6}$ M solution of 2 with 6 equivalents of Fe$^{2+}$ in CH$_2$Cl$_2$ at 298 (black line) and 283 K (red line).
4. Theoretical calculations

Several complexation environments were modelled using a mono- or a di-malonate derivative bearing short bppCOOR arms as in ligands 1 and 4 or long bppCH₂OR arms as in 2. The situations modelled include complex formation between the two bpp arms of a malonate branch (A), between bpp arms of two malonate branches (B) and between bpp arms of vicinal C₆₀ molecules (C) (Figure S33). Two BF₄⁻ counterions per complex formation were included for electroneutrality. Minimum-energy geometries and binding energies for the complexation process were calculated under the cost-effective GFN2-xTB approach using the Grimme’s xTB program. The GFN2-xTB method is based on a Hamiltonian similar to the well-known DFTB3, uses a minimal valence basis set centered on atoms (STO-mG), and includes the latest density-dependent D₄ dispersion correction. Binding energies (Table 1 in the main text) were calculated as the energy difference between products and reactants of the complexation process according to Scheme S5.

\[ \Delta E_{\text{bind}} = (E_{\text{complex}} + E_{6-\text{water}}) - (E_{\text{ligand}} + E_{\text{Fe(II)-water-BF}_{4}^-}) \]

**Scheme S5.** Calculation of the binding energy of the Fe(II) complex using six water molecules to solvate the Fe²⁺ ion and two BF₄⁻ counteranions to maintain the electroneutrality. Note that for intermolecular complexation C (Figure S33), the \( E_{\text{ligand}} \) term is multiplied by two, whereas in complexes of hexa-adducts 1 and 2 \( E_{6-\text{water}} \) and \( E_{\text{Fe(II)-water-BF}_{4}^-} \) are multiplied by six (Figure 4b).

Electronic structure calculations were performed under the density functional theory (DFT) framework by using the Gaussian-16.A02 suite of programs. Simplified complexes C0-2 (Figure S35) and their corresponding ligands L0-2 were modelled and their minimum-energy geometries were obtained at the B3LYP/def2-SVP/LANL2DZ(Fe) level of theory. Closed-shell low-spin (LS, \( 2S+1=1 \)) and open-shell high-spin (HS, \( 2S+1=5 \)) configurations were considered for the Fe(II) complexes by employing the restricted (R) and unrestricted (U) versions of the B3LYP functional, respectively, and a total charge of +2. Solvent effects were included by means of the self-consistent reaction field (SCRF) approach, with the polarizable continuum model (PCM) and dichloromethane as solvent. Table S1 collects the relative energy of HS complexes C0-2 with respect to the LS state in both vacuum and solvent.

Theoretical absorption spectra were obtained by calculating the 120 lowest-lying electronic excited states at the time-dependent DFT (TD-DFT) (U)B3LYP*/def2-
SVP/LANL2DZ(Fe) level of theory including solvent effects (PCM, dichloromethane). Note that the B3LYP* functional is a reparameterization of B3LYP with a reduced admixture of the Hartree–Fock (HF) exchange (15%), optimal to alleviate the deficiencies of DFT in calculating the energy difference between the ground state and the lowest-lying excited states of iron pseudo-octahedral complexes. For Fe(II) complexes in the LS state, singlet → singlet (S₀ → Sₙ) electronic transitions were calculated at the geometry optimized for the LS electronic ground state S₀ (Figure S36). In the HS state, quintuplet → quintuplet (Q₀ → Qₙ) electronic transitions were calculated using the UB3LYP geometry optimized for the lowest-energy quintuplet Q₀ (Figure S36). The theoretical simulation of the absorption spectra (Figure 5a in the main text and Figure S37) was obtained by convoluting the electronic transitions with Gaussian functions of full-width-at-half-maximum of 0.1 eV. The nature of the most relevant electronic excitations was assessed by calculating the corresponding natural transition orbitals (NTOs) (Figures S38-S43). The absorption spectrum in a simulated titration experiment was obtained by weighting the initial (ligand L₁ or L₂) and final (complex C₁ and C₂) spectra from 1 to 0 and from 0 to 1, respectively, in steps of 0.1 (Figure 5b and 5c in the main text). To calculate the spectra, the experimentally estimated ratio of 100:0 and 25:75 for LS:HS was used in C₁ and C₂, respectively.

The relative position of the ground state and the lowest-lying singlet/triplet excited states was calculated for ligands L₀–1 and complexes C₀–2 systems in their LS state at the TD-B3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM (Table S2). The geometry of the lowest-energy singlet (S₁) and triplet (T₁) excited states was fully optimized by using the time-dependent approach along with the OPT keyword of Gaussian16-A03 at the TD-B3LYP/def2-SVP/LANL2DZ(Fe) level.

Theoretical simulations of the Raman spectra (Figure S50) were obtained by performing frequency calculations at the BHandHLYP/def2-SVP/LANL2DZ(Fe) level of theory. Raman-active vibrational modes were represented by means of the Chemcraft software.
Figure S33. Minimum-energy structures calculated at the GFN2-xTB level of theory for configurations A, B and C of Fe(II) complexes bearing short bppCOOR ligands as in 1 and 4 (top) and long bppCH₂OR ligands as in 2 (bottom).

Figure S34. Tilted (top) and lateral (bottom) views of the minimum-energy coordination environment calculated at the GFN2-xTB level for configuration A of the mono-malonate complexes formed by the bppCOOR ligand (a) and the bppCH₂OR ligand (b).
Figure S35. Representation of the model Fe(II) complexes C0-2 and their respective bpp (L0), bppCOOEt (L1) and bppCH2OCOCH3 (L2) ligands.

Figure S36. B3LYP/def2-SVP/LANL2DZ(Fe) minimum-energy structures calculated for Fe(II) complexes C0-2 in their low-spin and high-spin configurations. Coordination bond distances (in Å) are indicated.
Table S1. Energy of the high-spin state relative to the low-spin state (in eV) calculated for complexes C0-2 at the B3LYP/def2-SVP/LANL2DZ(Fe) level of theory in vacuum and including solvent effects (dichloromethane).

<table>
<thead>
<tr>
<th></th>
<th>Vacuum</th>
<th>Solvent (DCM)</th>
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<tbody>
<tr>
<td>C0</td>
<td>−0.0388</td>
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</tr>
<tr>
<td>C1</td>
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<td>C2</td>
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Figure S37. Theoretical absorption spectra calculated for a) L1/C1 and b) L2/C2, at the (U)B3LYP*/def2-SVP/LANL2DZ(Fe) level including solvent effects. The spectra of complexes C1 and C2 are computed for both low-spin (LS) and high-spin (HS) states.
Figure S38. Natural transition orbitals (NTOs) that describe the nature of the most-intense $S_0 \rightarrow S_n$ electronic excitations calculated at the TD-DFT B3LYP*/def2-SVP level in DCM for ligand L1 (Figure S37a, black line).

Figure S39. Natural transition orbitals (NTOs) that describe the nature of the most-intense $S_0 \rightarrow S_n$ electronic excitations calculated at the TD-DFT B3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM for complex C1(LS) (Figure S37a, green line).
Figure S40. Natural transition orbitals (NTOs) that describe the nature of the most-intense $Q_0 \rightarrow Q_n$ electronic excitations calculated at the TD-DFT UB3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM for complex C1(HS) (Figure S37a, red line).
**Figure S41.** Natural transition orbitals (NTOs) that describe the nature of the most-intense $S_0 \rightarrow S_n$ electronic excitations calculated at the TD-DFT B3LYP*/def2-SVP level in DCM for ligand L2 (Figure S37b, black line).

**Figure S42.** Natural transition orbitals (NTOs) that describe the nature of the most-intense $S_0 \rightarrow S_n$ electronic excitations calculated at the TD-DFT B3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM for complex C2(LS) (Figure S37b, green line).
Figure S43. Natural transition orbitals (NTOs) that describe the nature of the most-intense $Q_0 \rightarrow Q_n$ electronic excitations calculated at the TD-DFT UB3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM for complex C2(HS) (Figure S37b, red line).
Table S2. Energy difference (in eV) between the first singlet ($S_1$) and triplet excited state ($T_1$) and the ground state ($S_0$) at the various potential energy wells of ligands $L_0$–$L_2$ and complexes $C_0$–$C_2$ systems in their LS state at the B3LYP*/def2-SVP/LANL2DZ(Fe) level in DCM.

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<th>$E_3$ ($T_1$-$S_0$)</th>
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5. **Studies in the solid state**

5.1 Precipitation procedure for 5 and 6 and general characterization

**Synthesis of 5**: In a glovebox, 1 (25 mg, 0.005 mmol) was dissolved in 0.8 mL of dry dichloromethane. After this, Fe(BF$_4$)$_2$ was added in a MeCN solution (6.25 mL, 9.6 mM). After the addition of the iron salt, an instantaneous change of color from orange to red takes place. The solution was left stirring for 10 minutes and diethyl ether (40 mL) was added giving rise to a jelly red precipitate. The precipitate was washed several times with diethyl ether and dried in air to yield a homogeneous dark red powder ($m_{\text{prod}} = 21.3$ mg, yield 57%). Elemental analysis calcd for [(Fe(BF$_4$)$_2$)$_6$C$_{270}$H$_{192}$N$_{60}$O$_{48}$H$_2$O$_{60}$]: C 43.19, N 11.20; found: C 43.23, N 10.74, H 3.91.

**Synthesis of 6**: In a glovebox, 2 (25 mg, 0.0041 mmol) was dissolved in 0.8 mL of dry dichloromethane. After this, Fe(BF$_4$)$_2$ was added in a MeCN solution (5.2 mL, 9.6 mM). After the addition of the iron salt, an instantaneous change of color from orange to yellow takes place. The solution was left stirring for 10 minutes and diethyl ether (40 mL) was added giving rise to a yellow precipitate. The precipitate was washed several times with diethyl ether and dried in air to yield a homogeneous yellow powder ($m_{\text{prod}} = 16.8$ mg, yield 52%). Elemental analysis calcd for [Fe(BF$_4$)$_2$]$_6$C$_{318}$H$_{264}$N$_{60}$O$_{72}$ (H$_2$O)$_{20}$: C 48.87, N 10.75, H 3.92; found: C 49.02, N 10.15, H 3.81.

Elemental analysis was consistent with the presence of 60 or 20 water molecules (see above). The thermogravimetric analysis (TGA) of 5 (Figure S44) shows a weight loss of solvent molecules at 110 °C (13 %), which is consistent with the loss of 60 water molecules (expected weight loss of 14 %). Complex 6 shows a different behavior, a gradual weight loss starts at 30 °C until a sharp decrease occurs at 230 °C. The weight loss until this point (4.9%) agrees with the expected loss of 20 water molecules (4.6%). The IR spectrum of 5 presents the characteristic bands of BF$_4^-$ counteranions and those assigned to aromatic C=N and C=C bonds from the bpp units between 1500 and 1700 cm$^{-1}$ (Figure S45). XPS spectra of 5 and 6 confirmed the presence of all the expected atoms (Fe, C, N, O, B and F) (Figures S46 and S47) and provide calculated ratios of 1:7.5:1.9:8 for Fe:N:B:F in 5 and 1:10.3:1.41:8.2 in 6. These results confirmed that the charge of Fe$^{2+}$ was compensated by the BF$_4^-$ counterions. Although the quantification of the Fe:N ratio is not accurate with this technique, the values obtained for both systems are consistent with the presence of two bpp units per iron atom (the expected Fe:N ratio is 1:10).

The electrospray ionization mass spectrometry (ESI-MS) spectra of the precipitate of 1 and 12 equivalents of Fe(ClO$_4$)$_2$ dissolved in a mixture of dimethylformamide and methanol showed the presence of several species with up to six Fe$^{2+}$ coordinated to 1 plus ClO$_4^-$ counteranions (being M the fullerene (C$_{270}$H$_{192}$N$_{60}$O$_{48}$). The isolated species were: 2550Da [M+2Fe]$^{2+}$, 2677Da [M+2Fe+2(ClO$_4$)]$^{2+}$, 2805Da[M+3Fe+4(ClO$_4$)]$^{2+}$, 1751Da [M+2Fe+(ClO$_4$)]$^3+$, 1836Da [M+3Fe+3(ClO$_4$)]$^3+$, 1921Da [M+4Fe+5(ClO$_4$)]$^3+$, 2006Da [M+5Fe+7(ClO$_4$)]$^3+$ and 2091Da [M+6Fe+9(ClO$_4$)]$^3+$. The spectra of the precipitate of 2 and 12 equivalents of Fe(BF$_4$)$_2$ dissolved in acetonitrile showed a similar behavior. Several species with up to six Fe$^{2+}$ coordinated to 2 plus counter anions were detected.
5.2 Physical characterization

Elemental analyses (C, H and N) were performed with a CE Instruments EA 1110 CHNS Elemental analyzer. TGA was performed in Mettler Toledo TGA/SDTA 851e Thermogravimetric and Differential Thermal Analyzer. IR measurements were performed in a Fourier Transformation-Infrared Spectrometer NICOLET 5700. XPS (K-ALPHA, Thermo Scientific) was used to analyze the surfaces of the samples. All spectra were collected using Al Kα radiation (1486.6 eV), monochromatized by a twin crystal monochromator. Magnetic measurements of 5 and 6 were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer with an applied magnetic field of 0.1 T. Solvated samples of 5 and 6 were deposited in the bottom of a glass tube and covered with the mother liquor. This tube was used as the sample holder. These samples were corrected from the diamagnetism of the compound and sample holder using Pascal constants and the magnetic properties of a sample holder containing only the mother liquor. Photomagnetic measurements were performed irradiating with a 30993 cylindrical Helium-Neon Laser system from Research Electro-Optics (red light, λ = 633 nm, optical power 12 mW cm⁻²) coupled via an optical fiber to the cavity of the SQUID magnetometer. It was verified that irradiation resulted in no significant change in magnetic response due to heating of the sample. The photomagnetic samples consisted of a thin layer of compound whose weight was corrected by comparison of a thermal spin crossover curve with that of a more accurately weighted sample of the same compound. Solvated samples were protected with an oil immediately after being extracted from the mother liquor. To estimate the HS Fe(II) fraction of these complexes we have assumed a contribution in χ_MT per HS Fe(II) of 3.5 emu K mol⁻¹, which is an average value taking into account that typical χ_MT values for this type of complexes range from 3.2 to 3.8 emu K mol⁻¹ depending on the orbital contribution.
Thermogravimetric analysis (TGA)

**Figure S44.** TGA analysis of 5 (dashed line) and 6 (solid line).
5.4 Infrared spectroscopy

Figure S45. Infrared spectra of 1 and 5 (a) and 2 and 6 (b).
5.5 X-ray photoemission spectroscopy (XPS)

Figure S46. XPS spectra of complex 5. Black dots represent the experimental spectrum.
Figure S47. XPS spectra of complex 6, black dots represent the experimental spectrum.
5.6 Magnetic properties of the filtered samples

Figure 7 shows the temperature dependence of $\chi_{MT}$ measured for desolvated samples of 5 and 6 measured in absence of a diethyl ether protecting layer or grease. Both samples exhibit a gradual and incomplete spin-crossover with temperature. For 5, previously heated at 400 K, the gradual decrease of $\chi_{MT}$ from 20.0 emu K mol$^{-1}$ at 400 K to 11.2 emu K mol$^{-1}$ at 50 K is consistent with a decrease of the HS fraction from around 90 to 50%. Higher $\chi_{MT}$ values in all the range of temperatures are obtained for a filtered sample of 6, in line with the higher HS fraction observed in solution for 2 coordinated to Fe$^{2+}$ and for both samples measured in contact with a diethyl ether protecting layer. Thus, $\chi_{MT}$ of 6 decreases from 21.7 emu K mol$^{-1}$ (~100 % HS fraction) at 300 K to 15.1 emu K mol$^{-1}$ at 50 K (~70 % HS fraction). The more pronounced decrease of $\chi_{MT}$ observed at lower temperatures for the two compounds is likely due to the zero-field splitting of Fe(II).

Magnetic measurements after irradiation with red light at 10 K were carried out, observing a partial LIESST effect in both samples. Irradiation with a 633 nm laser at 10 K leads to a drastic increase of the magnetic signal reaching saturation after ca. 1 h. An increase of $\chi_{MT}$ to reach a maximum value of 16.6 emu K mol$^{-1}$ (~80 % HS fraction) for 5 and 19.2 emu K mol$^{-1}$ (~90 % HS fraction) for 6 at around 40 K, reflecting a zero-field splitting of HS Fe(II), was observed. This suggests partial LS to HS photoconversion (see Figure 7).
5.7 Raman

**Figure S48.** Raman spectra of filtered samples of 5 (a) and 6 (b) complexes at different temperatures.
By using complex C0 as a simple model of the Fe(II)-complex with pristine bpp ligands, the Raman spectra for HS and LS states were calculated at the BHandHLYP/def2-SVP/LANL2DZ(Fe) level of theory (Figure S50). Theoretical calculations indicate that a Raman-active vibration in the 1000–1050 cm\(^{-1}\) region is predicted for both LS and HS configurations, which originates from a bpp ring breathing motion coupled with a stretching of the axial N–Fe–N coordination bonds (Figure S50b). Due to the different Fe–N bond distances in low and high-spin configurations, this Raman-active vibration is predicted to appear at smaller wavenumbers for the HS state (1010 cm\(^{-1}\)) than for the LS state (1041 cm\(^{-1}\)) (Figure S50a), which nicely supports the experimental analysis.
Figure S50. a) Theoretical Raman spectrum calculated for C0(LS) and C0(HS) at the BHandHLYP/def2-SVP/LANL2DZ(Fe) level. b) Representation of the Raman-active vibrational mode in the 1000-1050 cm⁻¹ region for the LS and HS states.
6. References


