



A novel class of tetrairon(III) single-molecule magnets with graphene-binding groups

Chiara Danieli^{a,*}, Andrea Cornia^a, Claudia Cecchelli^a, Roberta Sessoli^b, Anne-Laure Barra^c,
Glaucio Ponterini^a, Barbara Zangrando^a

^a Department of Chemistry and INSTM Research Unit, University of Modena and Reggio Emilia, Via G. Campi 183, 41100 Modena, Italy

^b Department of Chemistry and INSTM Research Unit, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

^c Grenoble High Magnetic Field Laboratory – CNRS, BP 166, 25 Avenue des Martyrs, 38042 Grenoble Cedex 9, France

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ABSTRACT

Tripods of general formula $R'-O-CH_2C(CH_2OH)_3$ are excellent site-specific ligands for the preparation of functionalized Fe_4 single-molecule magnets. Herein, we describe the synthesis and characterization of two novel complexes designed to bind graphene surfaces, in which the R group consists of an alkyl spacer $-(CH_2)_n-$ ($n = 6$ and 10) and a terminal pyrenyl moiety. The site-specific ligand substitution on $[Fe_4(O-Me)_6(dpm)_6]$ (Hdpm = dipivaloylmethane) with the new tripods has been studied with 2H NMR on isotopically-enriched samples, revealing that, once formed, these clusters are stable in solution over long timescales. It was not possible to isolate the new compounds as crystalline solids, nevertheless they were chemically characterized by elemental analysis and 1H NMR. The presence of the pyrenyl ending groups prompted us to investigate the effect of metal complexation on fluorescence, and a full pyrene-to-iron cluster excitation energy transfer was observed. The analysis of the magnetic behaviour revealed an $S = 5$ ground spin state with a negative zero-field splitting parameter $D = -0.42 \text{ cm}^{-1}$.

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1. Introduction

Tetrairon(III) complexes with a propeller-like structure (also known as “ferric stars”) are among the most appealing single-molecule magnets (SMM) for application in molecular spintronics and quantum computing [1]. Since the discovery of the archetypal tetrairon(III) SMM, the compound $[Fe_4(OMe)_6(dpm)_6]$ [2] (**1**, Hdpm = dipivaloylmethane), several derivatives have been obtained by selective replacement of the six methoxide bridges with tripods $H_3L = R-C(CH_2OH)_3$. The products of the reaction are usually obtained as pure, crystalline materials and display enhanced magnetic properties as compared with the parent compound **1**. Moreover, the R group can be chosen so as to bring additional functionalities, such as surface-binding capability [3–7]. We have recently shown that tetrairon(III) SMM can be successfully anchored to native gold surfaces by using R groups containing thioacetyl moieties, with full retention of magnetic properties [8]. In a different approach, tripods bearing a terminal double bond were reacted with H-terminated silicon substrates to give arrays of molecular receptors designed for SMM binding [7]. The first CNT-

SMM hybrids (CNT = carbon nanotube) were also successfully realized by exploiting the noncovalent π -stacking interaction between pristine CNT and a Fe_4 derivative functionalized with pyrenyl units [9]. The tripodal ligand used (**H₃C4**, Scheme 1) is a derivative of pentaerythritol and comprises a short C4 alkyl spacer. In the present work we wish to describe the synthesis of two additional pyrene-functionalized SMM, **2** and **3**, bearing longer spacers (**H₃C6** and **H₃C10** in Scheme 1). The new compounds were characterized with NMR and fluorescence spectroscopy, and the magnetic properties were measured with DC magnetometry and HF-EPR spectroscopy.

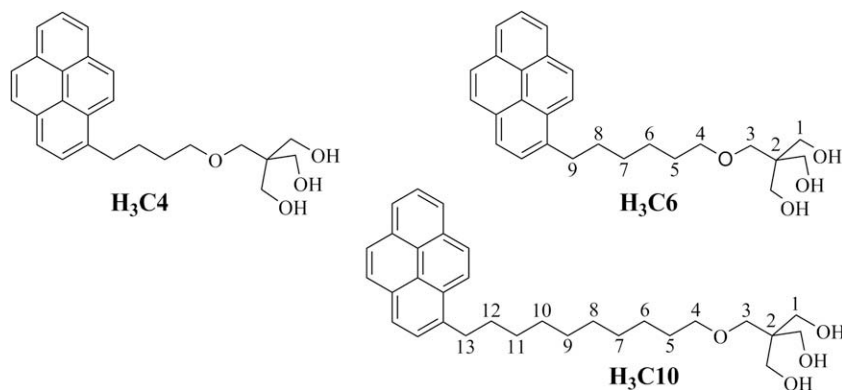
2. Experimental

2.1. Materials and methods

All the chemicals were of reagent-grade quality and used as received, unless otherwise stated. Anhydrous THF and diethyl ether, predried over $CaCl_2$, were distilled from Na/benzophenone shortly before use. MeOH was carefully dried by treatment with Mg/I_2 and distilled prior to use. Anhydrous toluene, *n*-hexane, dichloromethane (DCM) and 1,2-dichloroethane (DCE) were obtained by distillation over CaH_2 . Toluene and *n*-hexane were stored over Na wires, while DCM and DCE were stored over 4-Å molecular sieves in the dark.

* Corresponding author. Tel.: +39 59 2055030; fax: +39 59 373543.

E-mail addresses: cdanieli@unimore.it (C. Danieli), acornia@unimore.it (A. Cornia), roberta.sessoli@unifi.it (R. Sessoli), anne-laure.barra@grenoble.cnrs.fr (A.-L. Barra).



Scheme 1. Tripodal ligands functionalized with pyrenyl moieties.

(1-Methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol [10], 6-bromohexanoyl chloride [11], 10-bromodecanoyl chloride [12], $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ (**1**) [3], and $[\text{Fe}_4(\text{OMe})_6(\text{dpm}-d_{18})_6]$ (**1-d**) [3] were synthesized according to literature procedures.

All the solutions used for NMR and fluorescence experiments were prepared with anhydrous solvents and were stored excluding any possible contamination. The NMR spectra were recorded at 302 K with a Bruker FT-DPX200 NMR spectrometer. Proton chemical shifts are reported relative to TMS, while deuterium chemical shifts are referenced to acetone- d_6 , as external standard ($\delta = 2.16$ ppm). The protons of the pyrenyl ring are abbreviated as CHPy. ESI Mass spectra were obtained with an ESI Waters ZQ-4000 instrument; C, H analysis was performed using a Carlo Erba EA1110 CHNS-O automatic analyser.

2.2. Synthesis of the compounds

2.2.1. 6-Bromo-1-(pyren-1-yl)hexan-1-one (**4**)

Pyrene (2.478 g, 12.25 mmol) and 6-bromohexanoyl chloride (2.180 g, 10.21 mmol) were dissolved in 29 mL of anhydrous DCE under N_2 , the mixture was cooled to -10°C and AlCl_3 (1.633 g, 12.25 mmol) was added portionwise in 20 min. The reaction mixture turned to a dark color and was allowed to reach room temperature slowly and stirred overnight. Excess AlCl_3 was quenched with crushed ice, the resulting aqueous phase was saturated with solid NaCl, 50 mL of fresh DCE were added and the layers separated. The organic phase was washed with saturated NaCl, dried over MgSO_4 , filtered and concentrated in vacuo. The crude product was purified with column chromatography on silica gel (petroleum ether–DCM: 7:3) to yield **4** as a yellowish solid (3.014 g, 78%). ^1H NMR (CDCl_3): δ (ppm) 8.88 (d, $J = 9.4$ Hz, 1H, CHPy); 8.30–8.00 (m, 8H, CHPy); 3.44 (t, $J = 6.7$ Hz, 2H, CH_2Br); 3.21 (t, $J = 7.2$ Hz, 2H, CH_2CO); 2.02–1.82 (m, 4H, $\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_2\text{CH}_2\text{CO}$); 1.68–1.52 (m, 2H, CH_2). ^{13}C NMR (CDCl_3): δ (ppm) 206.60 (CO); 129.53 (CHPy); 129.43 (CHPy); 127.05 (CHPy); 126.38 (CHPy); 126.22 (CHPy); 125.97 (CHPy); 124.75 (CHPy); 123.99 (CHPy); 42.25 (CH_2); 33.55 (CH_2); 32.65 (CH_2); 27.93 (CH_2); 23.99 (CH_2).

2.2.2. 1-(6-Bromohexyl)pyrene (**5**)

To a stirred suspension of AlCl_3 (0.880 g, 6.60 mmol) in 9 mL of anhydrous Et_2O under N_2 , LiAlH_4 (6.6 mL, 1-M solution in Et_2O) was added dropwise. To the resulting milky reaction mixture, a solution of **4** (1.00 g, 2.64 mmol) in 12.5 mL of anhydrous DCM was slowly added dropwise. The reaction turned orange with a white precipitate and was stirred at room temperature for 1 h. Excess LiAlH_4 was quenched by careful addition of crushed ice, then 2.5-M HCl was added until acidic pH. The reaction was extracted

with Et_2O (2×50 mL), the combined organic phases were washed with saturated NaCl, dried over MgSO_4 , filtered and concentrated in vacuo to yield **5** as a yellow solid (0.864 g, 92%), which was used without further purification (98%+ from ^1H NMR). ^1H NMR (CDCl_3): δ (ppm) 8.29 (d, $J = 9.2$ Hz, 1H, CHPy); 8.20–7.96 (m, 7H, CHPy); 7.87 (d, $J = 7.8$ Hz, 1H, CHPy); 3.42 (t, $J = 6.7$ Hz, 2H, CH_2Br); 3.36 (t, $J = 7.7$ Hz, 2H, CH_2Py); 1.97–1.81, (m, 4H, $\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_2\text{CH}_2\text{Py}$); 1.59–1.50 (m, 4H, CH_2). ^{13}C NMR (CDCl_3): δ (ppm) 136.34 ($\text{C}^{\text{IV}}\text{Py}$); 130.93 ($\text{C}^{\text{IV}}\text{Py}$); 129.76 ($\text{C}^{\text{IV}}\text{Py}$); 127.51 (CHPy); 127.20 (CHPy); 127.16 (CHPy); 126.54 (CHPy); 125.77 (CHPy); 124.82 (CHPy); 124.77 (CHPy); 124.65 (CHPy); 123.39 (CHPy); 33.84 (CH_2); 33.40 (CH_2); 32.76 (CH_2); 31.63 (CH_2); 28.84 (CH_2); 28.09 (CH_2).

2.2.3. 2-(Hydroxymethyl)-2-((6-(pyren-1-yl)hexyloxy)methyl)propane-1,3-diol (**H₃C6**)

To a stirred suspension of NaH (0.289 g, 60% w/w dispersion in mineral oil, 12.0 mmol) in 17 mL of anhydrous THF under N_2 , (1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol (0.193 g, 1.20 mmol) was added as a solid in one portion. The mixture was stirred at room temperature for 1 h, then a solution of **5** (0.484 g, 1.32 mmol) in 7 mL of THF was added dropwise, followed by tetrabutylammonium bromide (TBABr) (0.020 g, 0.053 mmol). The reaction was stirred at room temperature for 3 days under N_2 , excess NaH was quenched with careful addition of MeOH, the solution was acidified with 2.5-M HCl until pH 1. The solvent was removed in vacuo and the crude material was purified with column chromatography on silica gel (DCM, gradient elution to DCM–MeOH: 10:1) to yield the intermediate monoacetylated product **AcH₂C6** (0.200 g, 0.432 mmol) and a small amount of the desired compound **H₃C6** (0.030 g, 6%). The monoacetylated product (0.200 g, 0.432 mmol) was dissolved in 4 mL of anhydrous MeOH, NaOMe (0.015 mL, 2.94-M solution in methanol, 0.044 mmol) was added and the mixture was stirred under N_2 for 1 day at room temperature. Finally, a drop of 2.5-M HCl was added and the solvent removed in vacuo to yield **H₃C6** as a light yellow solid (0.178 g, 98%).

^1H NMR for **AcH₂C6** (CDCl_3): δ (ppm) 8.29 (d, $J = 9.4$ Hz, 1H, CHPy); 8.20–7.95 (m, 7H, CHPy); 7.87 (d, $J = 7.8$ Hz, 1H, CHPy); 4.19 (s, 2H, CH_2OCO); 3.69–3.55 (m, 4H, CH_2OH); 3.43 (s, 2H, $\text{OCH}_2\text{C}^{\text{IV}}$); 3.42 (t, $J = 6.2$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{O}$); 3.36 (t, $J = 7.6$ Hz, 2H, CH_2Py); 2.08 (s, 3H, CH_3CO); 1.96–1.81 (m, 2H, CH_2); 1.66–1.38 (m, 6H, CH_2).

^1H NMR for **H₃C6** ($\text{DMSO}-d_6$): δ (ppm) 8.35–8.00 (m, 8H, CHPy); 7.92 (d, $J = 7.9$ Hz, 1H, CHPy); 4.15 (t, $J = 5.3$ Hz, 3H, OH); 3.39 (d, $J = 5.3$ Hz, 6H, CH_2OH); 3.35–3.26 (m, 6H, CH_2OCH_2 , CH_2Py); 1.83–1.69 (m, 2H, CH_2); 1.55–1.25 (m, 6H, CH_2). ^{13}C NMR ($\text{DMSO}-d_6$): δ (ppm) 137.00 ($\text{C}^{\text{IV}}\text{Py}$); 130.85 ($\text{C}^{\text{IV}}\text{Py}$); 130.37 ($\text{C}^{\text{IV}}\text{Py}$);

129.10 (C^{IV}Py); 127.96 (C^{IV}Py); 127.39 (CHPy); 127.34 (CHPy); 127.09 (CHPy); 126.33 (CHPy); 126.01 (CHPy); 124.83 (CHPy); 124.65 (CHPy); 124.20 (C^{IV}Py); 123.37 (CHPy); 70.71 (CH₂O); 69.62 (CH₂O); 61.00 (CH₂OH); 45.43 (C^{IV}); 32.51 (CH₂); 31.46 (CH₂); 29.06 (CH₂); 28.82 (CH₂); 25.52 (CH₂).

Anal. Calc. for **H₃C6**, C₂₇H₃₂O₄: C, 77.11; H, 7.67. Found: C, 76.77; H, 8.01%.

2.2.4. [Fe₄(C6)₂(dpm)₆] (**2**)

To a stirred solution of **1** (0.075 g, 0.050 mmol) in 20 mL of dry toluene, **H₃C6** (0.052 g, 0.12 mmol) was added and the resulting mixture was stirred for 40 h. The solvent was carefully removed in vacuo without warming, the resulting dark orange solid was stirred with 10 mL of anhydrous *n*-hexane for 30 min, and the suspension obtained was filtered on a G4 sintered glass frit. Removal of the solvent in vacuo without warming afforded **2** as a dark orange solid (0.081 g, 75%).

Anal. Calc. for **2**·C₆H₁₄, Fe₄O₂₀C₁₂₆H₁₈₆: C, 67.41; H, 8.37. Found: C, 67.35; H, 8.37%.

2.2.5. 10-Bromo-1-(pyren-1-yl)decan-1-one (**6**)

Pyrene (2.430 g, 12.00 mmol) and 10-bromodecanoyl chloride (2.700 g, 10.00 mmol) were dissolved in 28 mL of anhydrous DCE under N₂, the mixture was cooled to 0 °C and AlCl₃ (1.600 g, 12.00 mmol) was added portionwise in 20 min. The reaction turned to a dark color and was allowed to reach room temperature slowly and stirred overnight. Excess AlCl₃ was quenched with crushed ice, the resulting aqueous phase was saturated with solid NaCl, 50 mL of fresh DCE were added and the layers separated. The organic layer was washed with saturated NaCl, dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified with column chromatography on silica gel (petroleum ether–DCM: 7:3) to yield **6** as a yellow solid (3.450 g, 83%). ¹H NMR (CDCl₃): δ (ppm) 8.88 (d, *J* = 9.4 Hz, 1H, CHPy); 8.30–7.98 (m, 8H, CHPy); 3.39 (t, *J* = 6.8 Hz, 2H, CH₂Br); 3.19 (t, *J* = 7.3 Hz; 2H, CH₂CO); 1.94–1.76 (m, 4H, CH₂CH₂Br, CH₂CH₂CO); 1.53–1.31 (m, 10H, CH₂). ¹³C NMR (CDCl₃): δ (ppm) 205.25 (CO); 133.53 (C^{IV}Py); 132.91 (C^{IV}Py); 131.08 (C^{IV}Py); 130.56 (C^{IV}Py); 129.42 (CHPy); 129.32 (CHPy); 129.23 (C^{IV}Py); 127.04 (CHPy); 126.33 (CHPy); 126.15 (CHPy); 125.95 (CHPy); 125.91 (CHPy); 124.82 (CHPy); 124.35 (C^{IV}Py); 123.98 (CHPy); 42.63 (CH₂CO); 33.96 (CH₂Br); 32.81 (CH₂); 29.35 (CH₂); 29.25 (CH₂); 28.68 (CH₂); 28.13 (CH₂); 24.97 (CH₂).

2.2.6. 1-(10-Bromodecyl)pyrene (**7**)

To a stirred suspension of AlCl₃ (0.919 g, 6.90 mmol) in 9 mL of anhydrous Et₂O under N₂, LiAlH₄ (6.90 mL, 1-M solution in Et₂O) was added dropwise. To the resulting milky reaction mixture, a solution of **6** (1.20 g, 2.76 mmol) in 8 mL of anhydrous DCM was slowly added dropwise. The reaction turned orange with a white precipitate and was stirred at room temperature for 2 h. Excess LiAlH₄ was quenched by careful addition of crushed ice, then 2.5-M HCl was added until acidic pH. The reaction was extracted with Et₂O (2 × 50 mL), the combined organic phases were washed with saturated NaCl, dried over MgSO₄, filtered and concentrated in vacuo to yield **7** as a yellow solid (1.142 g, 98%), which was used without further purification (98% + from ¹H NMR). ¹H NMR (CDCl₃): δ (ppm) 8.31 (d, *J* = 9.4 Hz, 1H, CHPy); 8.21–7.97 (m, 7H, CHPy); 7.88 (d, *J* = 7.8 Hz, 1H, CHPy); 3.41 (t, *J* = 6.4 Hz, 2H, CH₂Br); 3.36 (t, *J* = 7.8 Hz, 2H, CH₂Py); 1.96–1.78 (m, 4H, CH₂CH₂Br, CH₂CH₂Py); 1.59–1.24 (m, 12H, CH₂). ¹³C NMR (CDCl₃): δ (ppm) 137.30 (C^{IV}Py); 131.52 (C^{IV}Py); 131.00 (C^{IV}Py); 129.75 (C^{IV}Py); 129.46 (C^{IV}Py); 128.66 (C^{IV}Py); 127.57 (CHPy); 127.23 (CHPy); 127.11 (CHPy); 126.51 (CHPy); 125.76 (CHPy); 124.80 (CHPy); 124.64 (CHPy); 123.53 (CHPy); 34.00 (CH₂Br); 33.61 (CH₂); 32.88 (CH₂); 31.93 (CH₂); 29.80 (CH₂); 29.56 (CH₂); 29.52 (CH₂); 29.44 (CH₂); 28.78 (CH₂); 28.20 (CH₂).

2.2.7. 2-(Hydroxymethyl)-2-((10-(pyren-1-yl)decyloxy)methyl)propane-1,3-diol (**H₃C10**)

To a stirred suspension of NaH (0.716 g, 60% w/w dispersion in mineral oil, 17.9 mmol) in 25 mL of anhydrous THF under N₂, (1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol (0.287 g, 1.79 mmol) was added as a solid portionwise. The mixture was stirred at room temperature for 1 h, then a solution of **7** (0.834 g, 1.98 mmol) in 3 mL of THF was added dropwise, followed by TBABr (0.030 g, 0.079 mmol). The reaction was stirred at room temperature for 5 days under N₂, excess NaH was quenched with careful addition of MeOH, the solution was acidified with 2.5-M HCl until pH 1. The solvent was removed in vacuo and the crude material was purified with column chromatography on silica gel (DCM, gradient elution to DCM–MeOH: 1:1) to yield the intermediate monoacetylated product **AcH₂C10** (0.486 g, 0.937 mmol) and **H₃C10** (0.243 g, 28%). Compound **AcH₂C10** (0.486 g, 0.937 mmol) was dissolved in 9 mL of anhydrous MeOH, NaOMe (0.032 mL, 2.94-M solution in methanol, 0.094 mmol) was added and the mixture was stirred under N₂ for one day at room temperature, a drop of 2.5 M HCl was added and the solvent removed in vacuo to yield **H₃C10** as a dark yellow solid (0.437 g, 99%).

¹H NMR for **AcH₂C10** (CDCl₃): δ (ppm) 8.28 (d, *J* = 9.4 Hz, 1H, CHPy); 8.18–7.94 (m, 7H, CHPy); 7.86 (d, *J* = 7.8 Hz, 1H, CHPy); 4.20 (s, 2H, CH₂OCO); 3.71–3.57 (m, 4H, CH₂OH); 3.43–3.29 (m, 6H, OCH₂C^{IV}, CH₂CH₂O, CH₂Py); 3.04 (br s, 2H, OH); 2.09 (s, 3H, CH₃CO); 1.85–1.79 (m, 2H, CH₂CH₂Py); 1.60–1.29 (m, 14H, CH₂). ¹³C NMR (CDCl₃): δ (ppm) 171.65 (CO); 137.32 (C^{IV}Py); 131.47 (C^{IV}Py); 130.96 (C^{IV}Py); 129.68 (C^{IV}Py); 128.61 (C^{IV}Py); 127.52 (CHPy); 127.21 (CHPy); 127.07 (CHPy); 126.45 (CHPy); 125.74 (CHPy); 125.08 (C^{IV}Py); 124.76 (CHPy); 124.59 (CHPy); 123.51 (CHPy); 72.26 (CH₂); 72.06 (CH₂); 63.67 (CH₂); 63.35 (CH₂); 53.41 (C^{IV}); 44.67 (CH₂); 33.57 (CH₂); 31.91 (CH₂); 29.80 (CH₂); 29.55 (CH₂); 29.46 (CH₂); 29.39 (CH₂); 26.06 (CH₂); 20.80 (CH₃).

¹H NMR for **H₃C10** (DMSO-*d*₆) δ (ppm) 8.28 (d, *J* = 9.3 Hz, 1H, CHPy); 8.17–7.93 (m, 7H, CHPy); 7.85 (d, *J* = 7.9 Hz, 1H, CHPy); 3.70 (s, 6H, CH₂OH); 3.42 (s, 2H, OCH₂C^{IV}); 3.38 (t, *J* = 6.6 Hz, 2H, CH₂CH₂O); 3.33 (t, *J* = 7.8 Hz, 2H, CH₂Py); 3.12 (br s, 3H, OH) 1.93–1.78 (m, 2H, CH₂); 1.60–1.28 (m, 14H, CH₂). ¹³C NMR (CDCl₃) δ (ppm) 137.40 (C^{IV}Py); 131.56 (C^{IV}Py); 131.04 (C^{IV}Py); 129.78 (C^{IV}Py); 128.70 (C^{IV}Py); 127.62 (CHPy); 127.30 (CHPy); 127.15 (CHPy); 126.54 (CHPy); 125.82 (CHPy); 125.19 (C^{IV}Py); 124.85 (CHPy); 124.68 (CHPy); 123.60 (CHPy); 73.55 (CH₂O); 72.23 (CH₂O); 64.45 (CH₂OH); 44.98 (C^{IV}); 33.66 (CH₂); 32.00 (CH₂); 29.89 (CH₂); 29.63 (CH₂); 29.55 (CH₂); 29.48 (CH₂); 26.15 (CH₂).

Anal. Calc. for **H₃C10**, C₃₁H₄₀O₄: C, 78.11; H, 8.46. Found: C, 77.89; H, 8.76%.

2.2.8. [Fe₄(C10)₂(dpm)₆] (**3**)

To a stirred solution of **1** (0.080 g, 0.053 mmol) in 20 mL of dry toluene, **H₃C10** (0.063 g, 0.13 mmol) was added and the resulting mixture was stirred for 40 h. The solvent was carefully removed in vacuo without warming, the resulting dark orange solid was stirred with 12 mL of anhydrous *n*-hexane for 30 min, and the suspension obtained was filtered on a G4 sintered glass frit. Removal of the solvent in vacuo without warming afforded **3** as a dark orange solid (0.098 g, 81%).

Anal. Calc. for **3**·0.5C₆H₁₄, Fe₄O₂₀C₁₃₁H₁₉₅: C, 68.01; H, 8.50. Found: C, 67.54; H, 8.51%.

2.3. Fluorescence spectra

Fluorescence emission spectra were recorded with a Spex Jobin Yvon FluoroMax 2 spectrofluorometer, using a triangular cell and front-face irradiation. Spectral bandwidth was around 2 nm.

2.4. Magnetic measurements

DC magnetic data were recorded using a Cryogenic S600 SQUID magnetometer. The temperature dependence of the M/H ratio (assumed to correspond to the static susceptibility) was measured on 15.77- and 13.51-mg samples of **2** and **3**, respectively, in applied fields of 10 kOe from 300 to 30 K and of 1 kOe from 30 to 1.9 K to suppress saturation effects. The isothermal magnetization of the same samples was also measured at 1.9, 2.5 and 4.5 K in fields up to 50 kOe.

Data reduction was carried out using the following molecular weights and diamagnetic contributions (estimated from Pascal's constants): for **2**, 2244.24 and $-1408 \times 10^{-6} \text{ emu mol}^{-1}$ (corresponding to $2 \cdot \text{C}_6\text{H}_{14}$); for **3**, 2313.37 and $-1464 \times 10^{-6} \text{ emu mol}^{-1}$ (corresponding to $3 \cdot 0.5\text{C}_6\text{H}_{14}$).

2.5. EPR spectra

High-Frequency EPR (HF-EPR) spectra were recorded at the Grenoble High Magnetic Field Laboratory on a homebuilt spectrometer working in single-pass mode, at temperatures of 5, 10 and 20 K. Gunn diodes operating at 95 or 115 GHz, equipped with a frequency doubler were used as source excitation. The amorphous samples of **2** and **3** used for the experiments were crushed using a mortar and pestle and pressed in a pellet. Spin-Hamiltonian calculations and simulation of HF-EPR spectra were carried out as described elsewhere [5]. The uncertainty in the spin-Hamiltonian parameters obtained by simulation of HF-EPR spectra is of the order of ± 1 on the last significant digit.

3. Results and discussion

3.1. Synthesis

The two novel pyrenyl ligands were synthesised as shown in Scheme 2. Pyrene was acylated with the appropriate ω -bromoalkanoyl chloride through a classical Friedel-Crafts reaction [12,13]. The subsequent reduction of the carbonyl moiety was carried out in mild conditions [14] to give the corresponding 1-(ω -bromoalkyl)pyrene (**5**, **7**) in good yields without need of purification. The next step, i.e. the coupling reaction of 1-(ω -bromoalkyl)pyrene with (1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol, proved not to be trivial. Literature procedures employing KOH in DMSO [15,16] lead almost exclusively to the formation of elimination by-products. Strictly anhydrous conditions with NaH as base

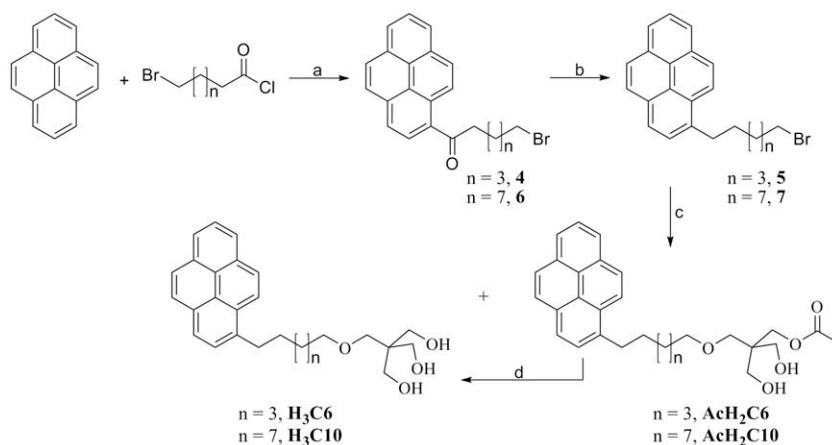
and catalytic TBABr proved to be the most successful strategy to the desired products. Interestingly, the work-up conditions allowed to isolate both the totally deprotected tripods and the monoacetylated derivatives, which were quantitatively hydrolyzed to give the target compounds **H₃C6** and **H₃C10**.

The coordinating ability of the two new ligands was tested using ^2H NMR. When samples are isotopically enriched on the *t*Bu groups of dpm^- ligands, the paramagnetically-shifted ^2H NMR signals allow to easily monitor structural changes in the tetrairon(III) core [3,5]. Toluene solutions of the deuterated complex $[\text{Fe}_4(\text{OME})_6(\text{dpm}-d_{18})_6]$ (**1-d**) showed time dependent ^2H NMR spectra, as previously reported for Et_2O solutions [3]. If spectra are recorded immediately after the dissolution two distinct signals appear at $\delta = 10.3$ and at 12.7 ppm in a 91:9 ratio, which are assigned respectively to the intact tetrairon(III) species and to a magnetically uncoupled $\text{Fe}(\text{dpm})$ complex. After 24 h, the latter signal is largely dominant and after 6 days dpm^- is present exclusively as monomeric $\text{Fe}(\text{dpm})$ complexes and as free ligand ($\delta = 0.9$ ppm) (Fig. 1a).

The above-described trend is drastically affected if an excess of tripodal ligand (2.7 eq.) is added to a 1.6 mM solution of **1-d** in toluene (see Fig. 1b and c). The ratio between the signals at 10.3 ppm and at 12.7 ppm is 4:1 short after preparation and raises to 7:1 after 24 h. After 6 days the spectra are dominated by the resonance from intact tetrairon(III) complexes, with only very weak signals at 12.7 ppm and at 0.9 ppm. Thus, the two tripods **H₃C6** and **H₃C10** show the same coordinating ability and stabilize tetrairon(III) complexes over long timescales. Indeed, very similar spectra were obtained using the shorter-chain ligand **H₃C4**, whose tetrairon(III) complex could be isolated in crystalline form [9].

To gain further evidence, the same solutions were analysed with ESI-MS, a unique tool for the determination of the molecular mass of large and labile molecules. The ESI (+) spectra revealed signals centred at $m/z = 2289$ and 2401, attributable to $[\mathbf{2-d} + \text{Na}^+]$ and $[\mathbf{3-d} + \text{Na}^+]$, respectively. A remarkable agreement between the theoretical masses and the reconstructed ESI isotope patterns was found, thus confirming the ^2H NMR data.

Unfortunately, all attempts to isolate product clusters in crystalline form failed. The complexes were thus assembled in dry toluene solution using excess ligand, the solvent was removed in vacuo and the solid was extracted with dry *n*-hexane, since the solubility of **H₃C6** and **H₃C10** in this solvent is as low as 10^{-5} M (data obtained by UV-Vis analysis of saturated solutions). Solvent removal from the filtered extracts led to **2** and **3** as dark orange amorphous solids in good yield.



Scheme 2. Synthesis of the ligands **H₃C6** and **H₃C10**. Experimental conditions: (a) AlCl_3 , DCE, -10 °C to room temperature, 18 h; (b) AlCl_3 , LiAlH_4 , $\text{Et}_2\text{O}/\text{DCM}$, 1–2 h room temperature; (c) (1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol, NaH, THF, TBABr, 3–5 days, room temperature and (d) NaOMe, MeOH, room temperature, 1 day.

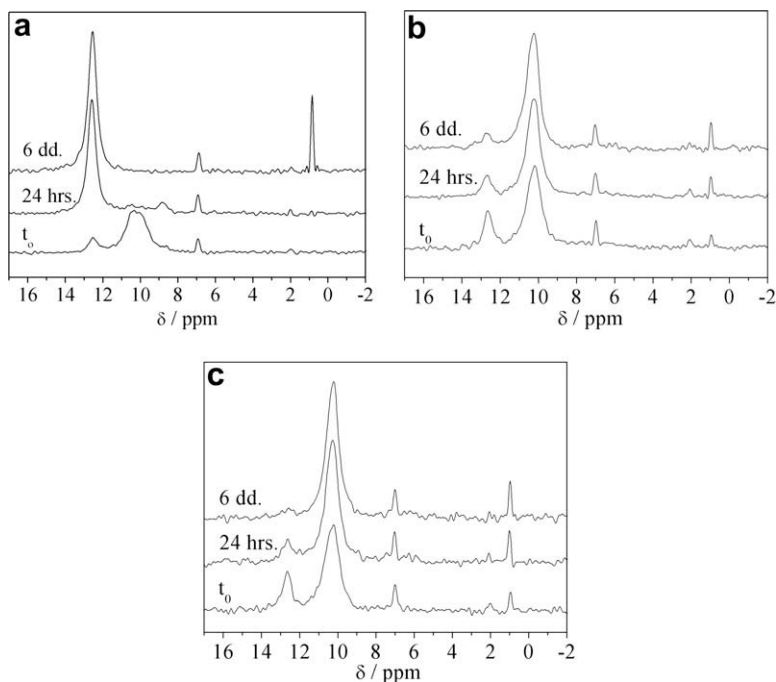


Fig. 1. Time-dependent ^2H NMR spectra of tetrairon(III) complexes in toluene solution at 302 K (t_0 labels freshly prepared solutions). (a) 1.57 mM solution of **1-d**. (b) 1.55 mM solution of **1-d** with addition of excess tripodal ligand **H₃C6**. (c) 1.64 mM solution of **1-d** with addition of excess tripodal ligand **H₃C10**.

3.2. Solution characterization

Tetrairon(III) clusters with general formula $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$, although strongly paramagnetic, exhibit a quite distinctive ^1H NMR resonance arising from *t*Bu protons, whose very broad signal is observed at ca. 10.4 ppm at room temperature. The tripodal ligands L^{3-} , when coordinated, do not show any observable NMR signal from ^1H nuclei lying closer to the metal centers, such as C1 hydrogens and the first few CH_2 groups of alkyl substituents (refer to Scheme 1 for the atom numbering) [5]. The ^1H NMR spectrum of **2** in toluene- d_8 is presented in Fig. 2a. In addition to the above-mentioned *t*Bu signal, the spectrum comprises a group of broad resonances at 7.93–7.70 ppm arising from the 18 aromatic protons of the pyrenyl rings, which display unresolved hyperfine splittings. In the spectral region spanned by C1, C3, C4 and C9 hydrogens of the free ligand ($\delta = 3.6$ –3.1 ppm), a broad signal is observed at 3.3 ppm, whose integrated intensity corresponds to four protons only. This resonance is assigned to C9 protons, which lie farthest from the metal centers (see Supporting Information for the ^1H NMR spectrum of **H₃C10** in toluene- d_8). Integration of the broad signal at 1.72–1.33 ppm also indicates that, beside C4,

additional protons of the aliphatic spacer escape NMR detection, thus lending further support to metal complexation. The longer alkyl spacer in **3** coherently affords sharper NMR resonances from pyrenyl and C13 hydrogens, as shown in Fig. 2b. Finally, traces of *n*-hexane are clearly detectable in both spectra (ca. 1.0 and 0.5 molecules per cluster for **2** and **3**, respectively).

Pyrenyl derivatives are widely used as fluorescent probe molecules for crucial applications, as chemosensors for metal ions [17], optical switches [18] and hybridization fluorescence sensors for polynucleotides [19], just to cite few. The fluorescence changes of pyrene hydroxamate derivatives due to metal ion complexation were studied in detail by Fages and coworkers. Complexation of iron(III) by a trichromophoric tripodal hydroxamate ligand was found to induce almost quantitative quenching of the fluorescence emission of the ligand [20].

The fluorescence spectra of dilute solutions of **H₃C6** and **H₃C10** (Fig. 3) in toluene show the monomer emission, patterned in five principal vibronic bands, while the broad excimer emission around 485 nm is almost not detectable, as expected for dilute solutions of pyrene derivatives. The relative intensity of peak III to peak I (see Fig. 3), known to be solvent sensitive, was found to be around

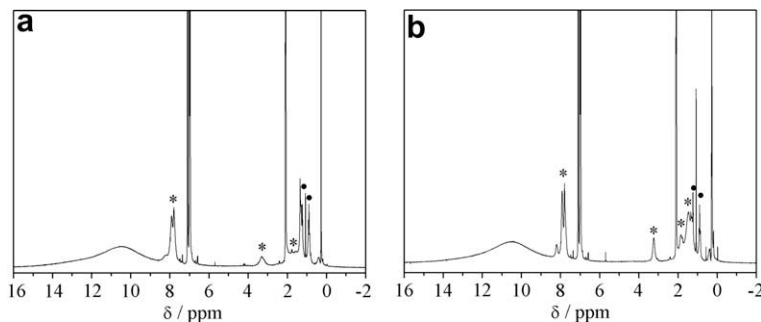


Fig. 2. ^1H NMR spectra of **2** (a) and **3** (b) in toluene- d_8 . The signals labelled with * are ascribed to tripodal ligands, while the signals marked with ● are due to traces of *n*-hexane.

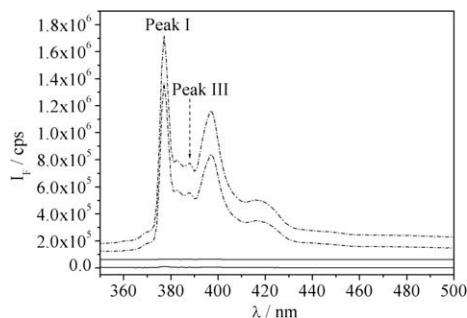


Fig. 3. Fluorescence spectra of 10^{-4} M solutions of **2** (grey, upper solid line) and **3** (black, lower solid line) in toluene. The fluorescence spectra of the free ligands H_2C6 (grey, upper dash-dot line) and H_3C10 (black, lower dash-dot line) are also reported for comparison at similar concentration (ligand and cluster samples were totally absorbing at $\lambda_{exc} = 300$ nm).

0.43, smaller than for toluene solutions of unsubstituted pyrene [21], but similar to the ratio found with other 1-substituted pyrene derivatives [22]. The spectra of **2** and **3** revealed a virtually complete excitation energy transfer (EET) from the S_1 state of pyrene to the chromophoric iron cluster ($\Phi_{EET} \geq 0.99$ for **2**, $\Phi_{EET} \sim 1$ for **3**, respectively, see Fig. 3). The residual very weak fluorescence might be attributed to traces of free ligand.

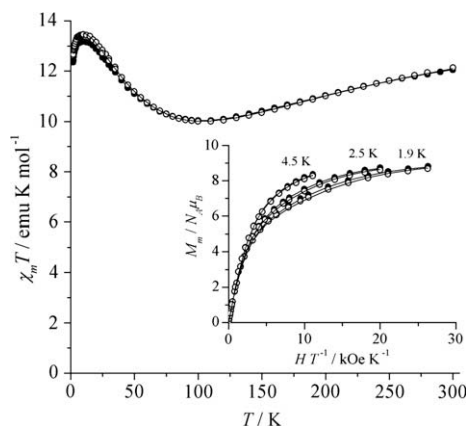


Fig. 4. DC magnetic properties of **2** (solid symbols) and **3** (void symbols). The solid lines provide the best fit to the experimental data with the following spin-Hamiltonian parameters: (for **2**) $J_1 = 13.79(2) \text{ cm}^{-1}$, $J_2 = -0.903(14) \text{ cm}^{-1}$, $g = 1.8782(5)$; (for **3**) $J_1 = 14.48(4) \text{ cm}^{-1}$, $J_2 = -0.46(2) \text{ cm}^{-1}$, $g = 1.8996(8)$. The inset shows isothermal magnetization data, along with the best-fit simulations obtained with (for **2**) $D = -0.349(4) \text{ cm}^{-1}$, $g = 1.852(3)$ and (for **3**) $D = -0.386(6) \text{ cm}^{-1}$, $g = 1.858(4)$. The spin-Hamiltonians used are defined in Ref. [5].

A full EET is consistent with the observation that the efficiency of quenching was independent of the length of the spacer alkyl chain.

3.3. Magnetic properties and HF-EPR spectra

The magnetic properties of **2** and **3** have been investigated using magnetic measurements and HF-EPR spectroscopy on powder samples. The $\chi_m T$ product of **2** and **3**, where χ_m is molar magnetic susceptibility and T is absolute temperature, is reported in Fig. 4 as a function of T . The overall trend is typical for tetrairon(III) propellers, the low- T increase of the magnetic moment being due to the selective population of the ground $S = 5$ state [3]. However, the maximum $\chi_m T$ value observed around 10 K in the two compounds is $13.2 \text{ emu K mol}^{-1}$ (**2**) and $13.4 \text{ emu K mol}^{-1}$ (**3**), hence ca. 10% lower than the Curie constant for an $S = 5$ spin state ($15.0 \text{ emu K mol}^{-1}$ with $g = 2.00$, as appropriate for high-spin iron(III)). The discrepancy, which exceeds the experimental accuracy of magnetic measurements, is confirmed by the unphysically low g values obtained by the quantitative analysis of $\chi_m T$ versus T and M_m versus H data (see caption to Fig. 4) using a well-established spin-Hamiltonian formalism [5]. The fit is otherwise excellent and affords spin-Hamiltonian parameters close to those observed in many other tetrairon(III) propellers [3,5]. It is likely that diamagnetic or weakly magnetic impurities arising from chemical manipulations contribute to decrease the magnetic response of the investigated samples, which are noncrystalline and difficult to purify.

Deeper insight was provided by the fine structure of the ground spin state as revealed by variable-temperature HF-EPR at 190 and 230 GHz. The spectra recorded at the higher frequency are gathered in Fig. 5, while 190-GHz spectra can be found in the Supporting Information. They are typical for high-spin species with an easy axis anisotropy [23] and can be accurately reproduced with the following spin-Hamiltonian parameters, as defined in Ref. [5]: for **2**, $D = -0.421 \text{ cm}^{-1}$, $E = 0.009 \text{ cm}^{-1}$, $B_4^0 = 1.8 \times 10^{-5} \text{ cm}^{-1}$; for **3**, $D = -0.422 \text{ cm}^{-1}$, $E = 0.008 \text{ cm}^{-1}$, $B_4^0 = 2.3 \times 10^{-5} \text{ cm}^{-1}$ ($S = 5$ and $g = 2.000 \pm 0.005$ throughout). Thus, the two complexes have identical magnetic anisotropy within experimental error. Furthermore, their spin-Hamiltonian parameters are typical for tetrairon(III) propellers $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$, in which the tripodal ligands adopt a $\eta^2, \eta^2, \eta^2, \mu_4$ coordination mode [3–7].

4. Conclusion

Two novel tetrairon(III) SMM designed to bind graphene surfaces through pyrenyl groups were synthesised using new tripodal ligands with spacers of different length. Although the new compounds could not be isolated as crystalline solids suitable for X-ray diffraction studies, their molecular structure was inferred from

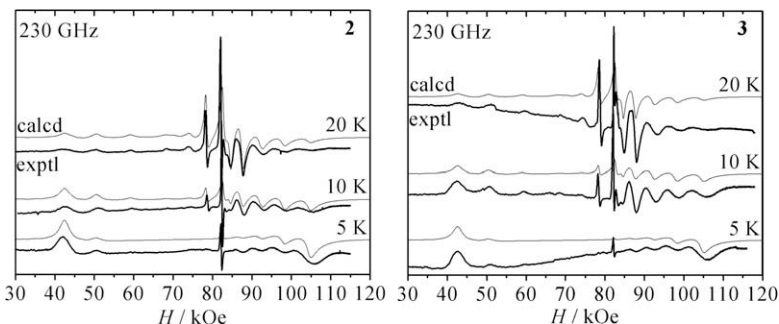


Fig. 5. HF-EPR spectra of **2** and **3** recorded at 230 GHz and at three different temperatures. The free electron resonance is found at $H_0 = 82.1 \text{ kOe}$. The thin lines are best-fit simulations obtained with the parameters reported in the text.

^1H NMR and fluorescence spectra, magnetic measurements and HF-EPR. In particular, the typical ground spin state of $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$ complexes ($S = 5$ with a negative D parameter) was clearly revealed by HF-EPR.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2008.12.024](https://doi.org/10.1016/j.poly.2008.12.024).

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