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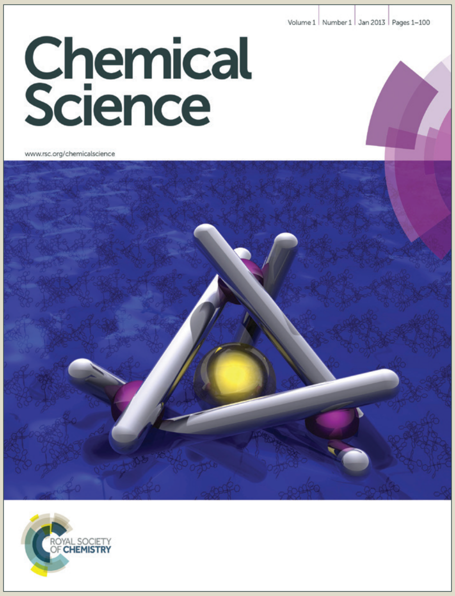

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Co-crystallized fullerene and mixed (phthalocyaninato)(porphyrinato) dysprosium double-decker SMM

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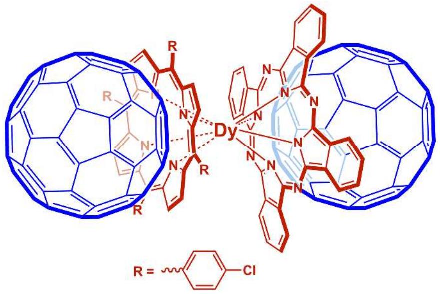
Effective and different inter-molecular interaction between fullerene C_{60} and tetrapyrrole-based double-decker SMM of three cocrystallates with different molar ratio rationalizes the slight structural change and different magnetic properties. The present result indicates that different integrating mode between the SMM molecule and conjugated sp^2-carbon substrate is able to affect the magnetic properties of the spintronic devices to different degree, representing the effort towards understanding the effect of the conjugated sp^2-carbon substrate on the magnetic property of SMM spintronic devices at the molecule level.

Introduction

Single molecule magnets (SMMs) with a wide range of unique functional properties including magnetic bistability, quantum tunneling of magnetization, and quantum coherence have attracted significant interests due to their potential applications in high-density information storage, quantum computing, and spintronics.[1,2] Considerable efforts have been devoted to correlating the relationship between the electronic structure of spin carrier and SMM properties aiming for improving their performance.[3] However, exploration to the interaction between SMM molecule with the macroscopic world (as one of important steps towards practical applications) has not been conducted in an extensive manner thus far with only a few pioneering trials in constructing spintronic devices with different kinds of substrates.[4,5] However, preliminary effort in organizing and addressing SMM molecules to understand the spin-transport mechanism has clearly revealed the advantage of conjugated carbon substrates like graphene and carbon nanotube as good integrating base due to their high mobility and long spin coherence lifetime and length.[4b,6]

For the purpose of realizing the SMM spintronic devices, bis(phthalocyaninato) terbium SMM with/without one pyrenyl substituent has been integrated on either graphene or carbon nanotube substrate *via* non-covalent π-π interaction since 2009.[7] The magnetization reversal of this double-decker SMM was successfully detected and the functionality in an original spin-valve also demonstrated.[8,9] However, due to the lack of the valid insight into the effective interaction between the double-decker molecule and conjugated carbon substrate at the molecule level, the effect of the conjugated substrate on the SMM behavior has not been exactly explored. Knowledge in this direction seems to be limited to the recognition of influence of the SMM properties by surroundings.[10] Investigation over the magnetic behavior of SMM molecules with effective and definite inter-molecular interaction with conjugated systems is therefore highly desired.



Scheme 1. Schematic molecular structures of mixed (phthalocyaninato)(porphyrinato) dysprosium double-decker compound and fullerene C_{60}.

Inspired with the disclosement of effective inter-molecular interaction between monomeric tetrapyrrole derivatives and C_{60},[11] much stronger interaction between fullerene and sandwich-type bis(tetrapyrrole) rare earth double-decker molecules is expected due to their well-fitted molecular structures,[12] Scheme 1. Previous studies over sandwich-type bis(tertrapyrrole) rare earth complexes revealed that the incorporation of both phthalocyanine and porphyrin ligands simultanously into the mixed-ring bis(tetrapyrrole) rare earth systems leads to optimized crystallinity over the homoleptic counterparts. As a consequence, mixed (phthalocyaninato)(porphyrinato) dysprosium double-decker SMM [Dy(Pc)(TClPP)] (**1**)[12b] was chosen to co-crystallize with fullerene C_{60} towards easy structural characterization by single crystal X-ray diffraction analysis. Fortunately, a series of three cocrystallates of [Dy(Pc)(TClPP)]·0.5C_{60}, [Dy(Pc)(TClPP)]·C_{60}, and [Dy(Pc)(TClPP)]·2C_{60} (**2-4**) were obtained, which also represent the first example of cocrystallates formed between sandwich-type bis(tetrapyrrole) complexes and fullerene. The effective and different inter-molecular interaction between fullerene and double-decker SMM in **2**-**4** was clearly revealed by the C_{60}-tetrapyrrole separation according to single crystal X-ray diffraction analysis result. This leads to obvious but different degree of decrease in the coordination interaction between the central metal ion and macrocycles in the three cocrystallates than that in **1**. Comparative theoretical calculations over the yttrium analogues [Y(Pc)(TClPP)]·2C_{60} and [Y(Pc)(TClPP)] not only confirm this result but also rationalizes the different SMM magnetic properties for the three cocrystallates. Nevertheless, due to the similar sp^2-carbon-based conjugated electronic structure of fullerene to graphene and in particular carbon nanotube, the present result appears to represent an initial step towards understanding and clarifying the effect of the conjugated carbon substrate on the property and functionality of SMM spintronic devices.

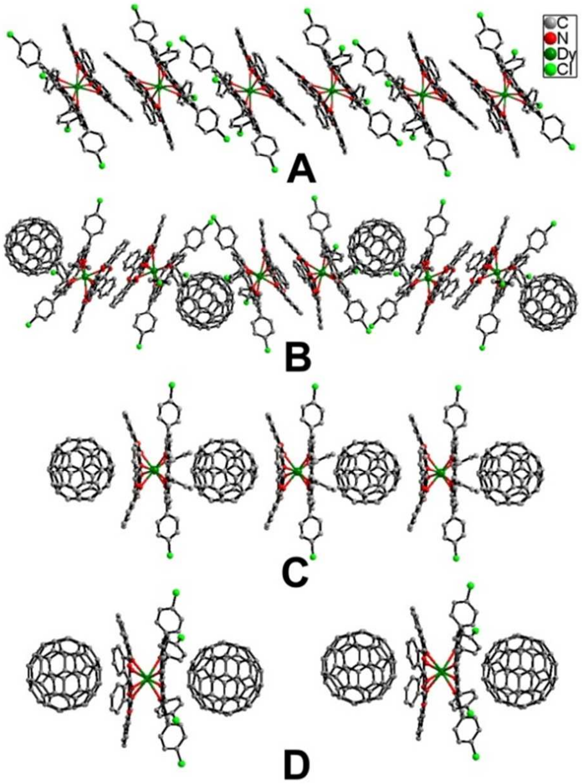


Fig. 1 Crystal structures of (A) [Dy(Pc)(TClPP)] (**1**), (B) [Dy(Pc)(TClPP)]·0.5C60 (**2**), (C) [Dy(Pc)(TClPP)]·C60 (**3**), and (D) [Dy(Pc)(TClPP)]·2C60 (**4**) with hydrogen atoms and solvent molecules omitted for clarity.

Results and discussion

Crystal structure of 1-4. As detailed in the previous literature,[12b] two neighboring double-decker molecules of **1** first form a supramolecular dimer *via* π-π interaction between the phthalocyanine ligands of the two double-decker molecules with the separation of two mean N4 planes of phthalocyanine ligands of 4.27 Å, which further connects to form a one-dimensional (1D) supramolecular chain *via* the C-H…π interaction between two TClPP rings of the adjacent dimers, Fig. 1a. However, in all the three cocrystallates composed of C_{60} and [Dy(Pc)(TClPP)] SMM with different molar ratio, the basic supramolecular structure changes to be the one with inclusion of C_{60} and the double-decker molecules, Figs. 1a-1c and S1a-S1c†, depending on the effective inter-molecular C_{60}-[Dy(Pc)(TClPP)] π-π and C-H…π interaction revealed by the very close separation of the 6:5 ring juncture of C_{60} and the mean N_4 plane of TClPP of double-decker in the value of *ca.* 2.90, 3.00, and 2.75 Å for **2**, **3**, and **4**, respectively, as well as that between C_{60} entity and the phthalocyanine chromophore of double-decker in **3** and **4** with the value of 3.00 and 3.10 Å, Table 1. The slight but obvious difference for the three cocrystallates indicates the difference in the inter-molecular C_{60}-[Dy(Pc)(TClPP)] interaction. Nevertheless, the effective inter-molecular interaction between C_{60} and double-decker molecule for cocrystallates **2**-**4** can also be clearly revealed by the intra-tetrapyrrole separation between the two mean N4 planes in double-decker molecule, which decreases from 2.76 Å in the pure double-decker compound **1** to 2.74 Å for **2**, 2.75 Å for **3**, and 2.72 Å for **4**. This different longitudinal contraction effect among **2**-**4** in turn accounts for their different magnetic properties and also relative to **1** as detailed below since pseudo-D_{4d} coordination geometry for the Dy ion in the double-decker molecule was disclosed for all the four compounds according to the twist angle (defined as the rotation angle of one coordination square away from the eclipsed conformation of the two squares), 43.60° for **1**, 44.45/41.22° for **2**, 44.41° for **3**, and 44.35° for **4**.

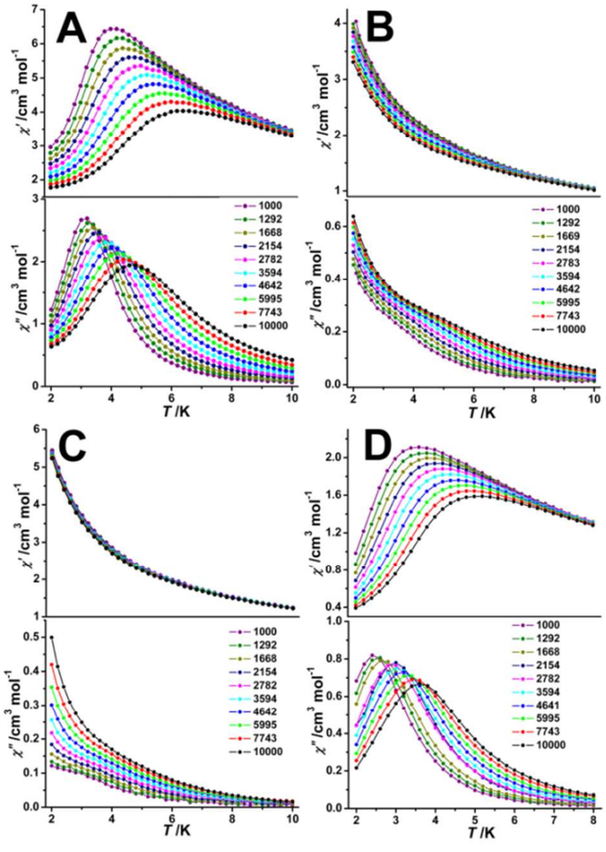


Fig. 2 Temperature dependence of χ′ and χ″ ac susceptibility of **1**-**4** (A-D) under zero dc field, respectively

Magnetic properties of 1-4. In line with the previous result,[12b] alternative current (ac) magnetic susceptibility measurement for pure double-decker compound **1** carried out in a zero dc magnetic field at 1000-10000 Hz instead of 10-997 Hz also discloses the frequency-dependent character of the out-of-phase signal (χ'') for this compound, Figs. 2 and S2†, confirming the nature of slow relaxation of magnetization as the typical characteristics of SMM. This is also true for the cocrystallates **2**-**4**, Figs. 2 and S2†. Nevertheless, as clearly shown in these figures, very clear peaks are observed in the χ'' vs T curves of **1** even at the frequency as low as 100 Hz, and the peaks for **4** are able to be observed only at relatively high frequency (actually above the frequency of 997 Hz), while no peak can be detected for **2** and **3** even at the frequency as high as 1000 Hz. These results certainly indicate the relatively stronger quantum tunneling of magnetization (QTM) for the double-decker SMM in **2**-**4** due to the effective inter-molecular interaction between C_{60} and [Dy(Pc)(TClPP)]. The present result also indicates that different integrating mode between the SMM molecule and conjugated sp^2-carbon substrate is able to affect the magnetic properties of the spintronic devices to different degree. Obviously, the difference in the inter-molecular interaction among the three cocrystallates induces the change in the electron distribution in the macrocyclic ligands and thus the decreased coordination interaction between the central metal ion and macrocycles, which should be responsible for the different QTM effect in **2**-**4** relative to **1**. This is further rationalized by comparative theoretical calculation over the electronic structures of $[Y(Pc)(TClPP)]{\cdot}2C_{60}$ and pure double-decker [Y(Pc)(TClPP)] as representatives of corresponding dysprosium species. On the basis of a thermally activated mechanism, $\tau = \tau_0\exp(U_{\mathrm{eff}}/kT)$ and $\tau = 1/(2\pi\nu)$, the Arrhenius law fitting for the data under zero dc magnetic field was carried out. As exhibited in Fig. 3, a linear relationship exists between $\ln(\tau)$ and $1/T$ in the temperature range of 2.0-4.0 K for **1** and **4**, which in turn results in a barrier $U_{\mathrm{eff}} = 16.9$ cm^{-1} (24.4 K) and $\tau_0 = 7.5 \times 10^{-8}$ s with $R = 0.997$ and $U_{\mathrm{eff}} = 13.1$ cm^{-1} (18.9 K) and $\tau_0 = 8.5 \times 10^{-8}$ s with $R = 0.999$, respectively, suggesting their thermal activated relaxation process for these two compounds. This is further supported by the one semi-circled Cole-Cole plots (χ'' *vs.* χ') obtained at 3.0, 4.0, and 5.0 K for **1** and **4**, Fig. S3†. On the basis of the Debye function[13] $\chi(\omega) = \chi_S + \dfrac{\chi_T - \chi_S}{1+(i\omega\tau_1)^{1-\alpha}}$ (**i**), the fitting leads to the following sets of parameters with α = 0.21-0.29 for **1** and α = 0.30 for **4**. These slightly big α parameters indicate the presence of the fast quantum tunneling of magnetization in addition to the slow magnetic relaxation in these two compounds.

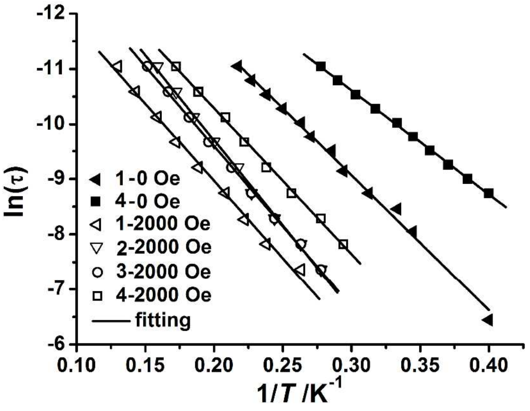


Fig. 3 The plots of ln(τ) vs. 1/*T* for **1** and **4** under zero dc field and **1**-**4** under 2000 Oe dc field.

To suppress the QTM effect caused by the intermolecular dipole-dipole interaction and provide more information about the SMM properties of **1**-**4**, a 2000 Oe external dc magnetic field was employed to suppress the QTM in ac magnetic susceptibility measurement with oscillating frequency at 1000-10000 Hz.[14] As expected, effective suppression on the QTM by external dc magnetic field added led to the observation of clear peaks in the χ'' vs T curves for both **2** and **3** which exhibit no peak in a zero dc magnetic field, Fig. 4. This is also true for the pure double-decker compound **1** and cocrystallate **4** as revealed by the observation of clear peaks in the χ'' vs T curves at decreased frequency of 100 Hz, respectively. Also by means of the Arrhenius law fitting method on the basis of corresponding data obtained under an external 2000 Oe field, Fig. 3, effective energy barrier of $U_{\mathrm{eff}} = 18.4\sim21.4$ cm^{-1} (26.5~30.9 K) for **1**-**4**, respectively, and $\tau_0 = 1.3\sim4.7 \times 10^{-7}$ s was obtained with $R = 0.998\sim0.999$. In addition, χ'' *vs.* χ' data at 5.0 K under 2000 Oe applied dc field give only one semi-circle. In particular, corresponding fitting based on the Debye function (**i**) gives α = 0.17~0.29 for all the four compounds **1**-**4**, Fig. S4†. These results reveal the existence of the sole thermal activated relaxation process remained for the double-decker SMM in **1**-**4** due to the suppression of the QTM process by the applied external static dc field. Herein, it is worth noting that the inter-molecular interaction between the SMM and fullerene seems to slightly affect the static magnetic properties of the cocrystallates **2**-**4** relative to that in **1** on the basis of the reported literature[12b] and Figs. S5 and S6†.

Correlation between the inter-molecular interaction in the cocrystallates and SMM properties. As revealed by single crystal X-ray diffraction analysis, the dysprosium ions in either **1** or cocrystallates **2**-**4** all employ the pseudo-D_{4d} coordination geometries in terms of the twist angle, indicating the less influence of coordination geometry on the SMM properties in the present case. In addition, structural analysis indicates that the nearest distance of the Dy…Dy in **3** (13.725 Å) is significantly longer than that in **4** (12.798 Å), Fig. S7†. This, however, is in good contrast to the severe QTM revealed for the former compound than the latter one, suggesting the non-dominant role of the dipole-dipole interactions in affecting the double-decker SMM properties. However, obviously different longitudinal contraction in the intra-tetrapyrrole separation between the two mean N4 planes in the double-decker molecule was revealed among **2**-**4** relative to that in **1** due to different intermolecular interactions between the fullerene and double-decker molecules. This is therefore attributed as the main factor in accounting for the different magnetic properties of the series of compounds. As a consequence, the coordination interaction intensity between the dysprosium ion and the two tetrapyrrole ligands in these four species is considered responsible for their different SMM properties as described above. With this in mind, density functional theory (DFT) studies over these two compounds were performed to confirm the hypothesis on the basis of the crystal structures of **1** and **4** as a typical representative of the three cocystallates (with the yttrium ion

Table 1. Crystallographic data and selected structural information for **1-4**.

	1	**2**	**3**	**4**
average Dy-N(TClPP) bond distance (Å)	2.43	2.43/2.43	2.42	2.43
average Dy-N(Pc) bond distance (Å)	2.46	2.46/2.45	2.47	2.45
Dy-N_4(Pc) plane distance (Å)	1.48	1.47/1.46	1.48	1.47
Dy-N_4(TClPP) plane distance (Å)	1.28	1.27/1.28	1.27	1.26
interplanar distance (Å)	2.76	2.74	2.75	2.73
dihedral angle between the two N_4 planes (°)	0.93	0.09/1.48	2.75	1.40
dihedral angle φ for the Pc ring (°)[a]	13.56~17.34	10.76~18.45	8.32~22.23	9.61~25.12
dihedral angle φ for the TClPP ring (°)[a]	6.13~18.94	5.65~18.53	9.52~10.48	5.48~18.70
twist angle (°)[b]	43.60	44.45/41.22	44.41	44.35
separation of mean N_4 plane of neighboring Pc (Å)	4.27	4.08	no	no
dihedral angle θ between the benzene rings and the TClPP N_4 plane (°)	60.16~73.73	58.89~76.57	58.88~67.02	58.17~63.90
separation of 6:5 ring juncture and mean N_4 plane of Pc (Å)	no	no	3.00	3.10
separation of 6:5 ring juncture and mean N_4 plane of TClPP (Å)	no	2.93/2.87	3.00	2.75

a The average dihedral angle of the individual pyrrole or isoindole ring with respect to the corresponding N4 mean plane.
b Defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles.

replacing the f-electron-involved dysprosium ion for the purpose of conducting calculations). Coordination attraction was revealed to actually consist of two components including the covalent part generated from the orbital coupling and the ionic part induced by the electrostatic attraction.[15] To unravel the nature of the coordination attraction between the dysprosium ion and the two tetrapyrrole macrocyclic ligands in pure double-decker and cocrystallates, natural bond orbital (NBO) calculations over the yttrium counterparts [Y(Pc)(TClPP)] (**1’**) and [Y(Pc)(TClPP)]·2C_{60} (**4’**) were carried out at the level of B97D/LanL2DZ.[16] The calculation results reveal that a total inter-molecular interaction energy in the trimeric entity including the inter-molecular double-decker-C_{60} π-π and C-H…π interaction energy as well as the electrostatic attraction between the double-decker moiety and C_{60} entities amounts as high as -37.6 kcal/mol, Fig. 5. This result is in line with that reported for the dimeric unit composed of one porphyrin and one C_{60} entity with the value of -16 to -18 kcal/mol, Fig. 5.[17] In addition, along with the introduction of C_{60}, the total bond order[18] of the yttrium atom in the double-decker molecule decreases from 2.218 for **1’** to 1.858 for **4’**, indicating the obviously weakened covalent part of the coordination attraction between yttrium atom and the two tetrapyrrole ligands in the cocrystallate, Fig. S8†. Meanwhile, calculation results also indicate the decrease in the electrostatic attraction between the yttrium atom and TClPP/Pc ligand from -5.6×10^{-3}/-4.7×10^{-3} a.u for **1’** to -5.1×10^{-3}/-4.2×10^{-3} a.u for **4’**, revealing the decrease in the ionic part of the coordination attraction between the yttrium atom and the two tetrapyrrole ligands also along with the introduction of C_{60}. As a result, significant decrease amounting *ca.* 20% and 10% in terms of valance part and electrostatic attraction, respectively, relative to that of pure double-decker occurs in the coordination interaction between the two tetrapyrrole ligands and the central yttrium ion along with the introduction of C_{60} due to the effective inter-molecular C_{60}-tetrapyrrole interaction(s). This should be also true for the dysprosium ion with strong single-

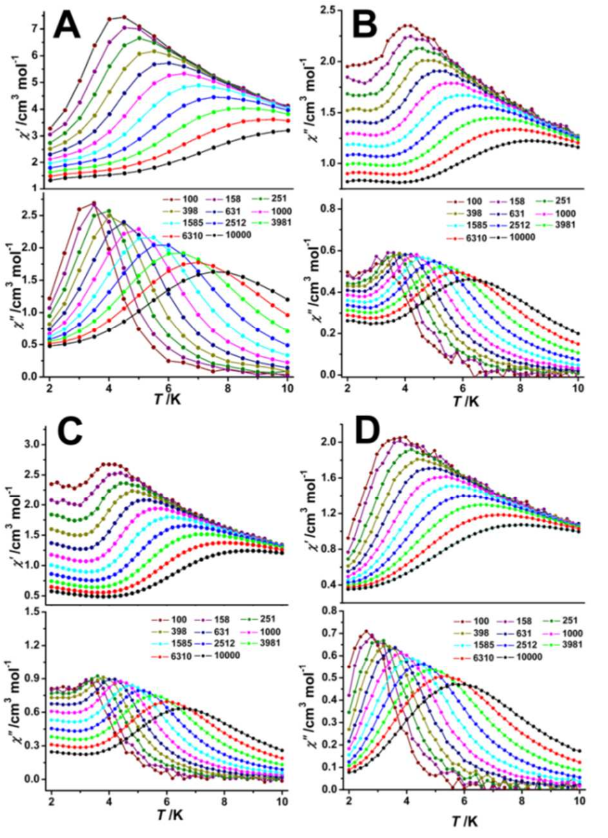


Fig. 4 Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility of **1** (A), **2** (B), **3** (C), and **4** (D) at the frequency from 100 to 10000 Hz under 2000 Oe dc field.

ion anisotropy in **4** relative to **1**, which may in turn results in a decrease in the uniaxial magnetic anisotropy of central lanthanide ion for the former compound relative to the latter one and is responsible for the different magnetic properties between **4** and **1**. This is also true for the **2** and **3** relative to **1**. Obviously, the presence of effective but different inter-molecular interaction between C_{60} and [Dy(Pc)(TClPP)] molecule in **2-4** as revealed above leads to obviously different longitudinal contraction effect in term of the intra-tetrapyrrole separation between the two mean N4 planes in double-decker molecule from 2.76 Å for **1** to 2.74 Å for **2**, 2.75 Å for **3**, and 2.72 Å for **4**, indicating the different intensity of coordination interaction between the tetrapyrrole ligands and dysprosium ion, which then accounts for the different magnetic properties of the double-decker SMM among these compounds.

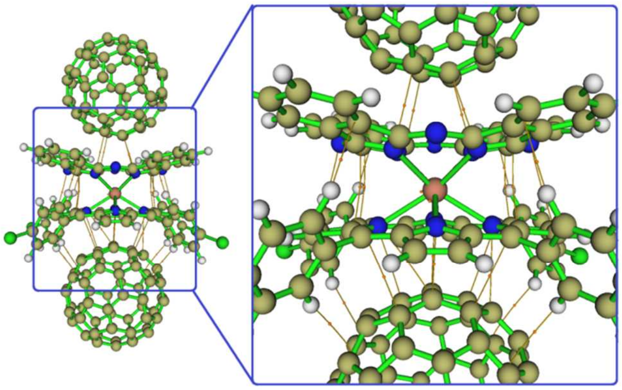


Fig. 5 Inter-molecular interaction between the C_{60} entities and [Y(Pc)(TClPP)] molecule.

Experimental

General remarks. All the reagents and solvents were used as received. The compound of sandwich-type neutral double-decker mixed (phthalocyaninato)(porphyrinato) dysprosium(III) [Dy(Pc)(TClPP)] (**1**) was prepared according to the published procedure.[19] Elemental analysis was performed on an Elementar Vavio El Ш. Magnetic measurements were performed on a Quantum Design MPMS XL-5 and PPMS-9T (EC-II) SQUID magnetometer on polycrystalline samples. Data were corrected for the diamagnetism of the samples using Pascal constants and of the sample holder by measurement. Crystal data of these three compounds **2-4** were collected on an Oxford Diffraction Gemini E diffractometer with Cu *Kα* radiation (λ = 1.5418 Å) at 120 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction, The structures were solved by the direct method (*SHELXS-97*) and refined by full-matrix least-squares (*SHELXL-97*) on F^2.[20] Anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. 'Crystallographic data and other pertinent information for all the complexes are summarized in Table S1†. CCDC 849698 for **1** (ref. 12b for detail) and 978330-978332 for **2-4**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [Dy(Pc)(TClPP)]·0.5C_{60} (2). Single crystals of cocrystallized fullerene-mixed(phthalocyaninato)(porphyrinato) dysprosium double-decker SMM **2** were obtained by simple diffusion of the *n*-hexane (15 mL) into the chloroform/o-dichlorobenzene (1:1) solution (5 mL) containing mixed (phthalocyaninato)(porphyrinato) dysprosium(III) complex [Dy(TClPP)(Pc)] (2.85 mg, 0.002 mmol) and C_{60} (11.52 mg, 0.016 mmol) with the yield of 1.3 mg, 32% (computed on the basis of the double-decker). Elemental analysis calcd (%) for $C_{106}H_{40}Cl_4DyN_{12}.(2CHCl_3)$ C 64.07, H 2.09, N 8.30; found: C 63.91, H 2.03, N 8.29.

Synthesis of [Dy(Pc)(TClPP)]·C_{60} (3). Single crystals of cocrystallized fullerene-mixed(phthalocyaninato)(porphyrinato) dysprosium double-decker SMM [Dy(Pc)(TClPP)]·C_{60} (**3**) were obtained by simple diffusion of the *n*-hexane (15 mL) into the chloroform/carbon disulfide (CS_2) (1:1) solution (5 mL) containing mixed (phthalocyaninato)(porphyrinato) dysprosium(III) complex [Dy(TClPP)(Pc)] (5.70 mg, about 0.004 mmol) and C_{60} (2.88 mg, 0.04 mmol) with the yield of 4.3 mg, 47%. Elemental analysis calcd (%) for $C_{136}H_{40}Cl_4DyN_{12}.(CHCl_3)$: C 72.63, H 1.82, N 7.42; found: C 72.61, H 1.83, N 7.46.

Synthesis of [Dy(Pc)(TClPP)]·2C_{60} (4). Single crystals of cocrystallized fullerene-mixed(phthalocyaninato)(porphyrinato) dysprosium double-decker SMM **1** were obtained by simple diffusion of the *n*-hexane (15 mL) into the chloroform/chlorobenzene (1:1) solution (4 mL) containing mixed (phthalocyaninato)(porphyrinato) dysprosium(III) complex [Dy(Pc)(TClPP)] (2.85 mg, 0.002 mmol) and C_{60} (2.88 mg, 0.004 mmol) with the yield of 1.8 mg, 27%. Elemental analysis calcd (%) for $C_{196}H_{40}Cl_4DyN_{12}.4(C_6H_5Cl)$: C 79.66, H 1.82, N 5.07; found: C 79.61, H 1.83, N 5.09.

Computational details. In order to confirm the hypothesis that the different magnetic properties for the double-decker SMM in the pure double-decker **1** and the three cocrystallates **2-4** originate from the effective π-π interaction between fullerene C_{60} and mixed (phthalocyaninato)(porphyrinato) dysprosium double-decker, comparative theoretical calculations over the electronic structures of the dimeric supramolecular structure [Dy(Pc)(TClPP)]·2C_{60} (**4**) and pure double-decker[Dy(Pc)(TClPP)] (**1**) as representative were carried out. Density functional theory (DFT) calculations of these two compounds were performed on the basis of the optimized crystal structures of **1** and **4** with the yttrium ion replacing the dysprosium ion. The total electron density and the fragment charge distribution of [Y(Pc)(TClPP)] (**1'**) and [Y(Pc)(TClPP)]·2C_{60} (**4'**) were calculated at the level of B97D/LanL2DZ.[16] In addition, coordination attraction has been revealed to actually consist of two components including the covalent part generated from the orbital coupling and the ionic part induced by the electrostatic attraction. The coordination attraction in term of covalent part could be evaluated by the total NBO bond order[21] and the electrostatic interaction between Pc (or TClPP) fragment and yttrium atom of double-deckers in **1'** and **4'** is calculated using the equation of $\sum_i \left(k\cos\theta \frac{q_i q_Y}{r_{iY}^2} \right)$, where q_i is the Hirshfeld charge[22] of any atom *i* belonging to Pc or TClPP rings, q_Y is the Hirshfeld charge of yttrium atom, and r_{iY} is the distance between *i* and yttrium atoms, and θ is the angle of atom i…Y…center of Pc (or TClPP) ligand. All calculations were carried out using the Gaussian 09 program[23] on an IBM P690 system housed at Shandong University.

Conclusions

Briefly summarizing above, systematic experimental and theoretical studies in a comparative manner over the structures and magnetic properties of sandwich-type tetrapyrrole-based dysprosium double-decker compound in a series of cocrystallates with fullerene clearly reveal the effects of effective and different inter-molecular interaction between C_{60} and [Dy(Pc)(TClPP)] SMM on the molecular structure, coordination interaction between the central metal ion and macrocycle rings, and magnetic properties. Due to the similar nature of sp^2-carbon-based conjugated electronic structure of fullerene to graphene and carbon nanotube, the present result represents the effort towards understanding and clarifying the effect of substrates on the property and functionality of SMM spintronic devices in particular those fabricated with sp^2-carbon substrate at the molecular level.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [temperature dependence of the χ' and χ'' ac susceptibility of **1**-**4** from 10 to 997 Hz under zero dc field, $\chi_M T$ *vs. T* curves, *M vs. H* curves, selected structural information, crystal data and structure refinement for **2**-**4**, and mayer bond order of **1'** and **4'**]. See DOI: 10.1039/b000000x/

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