Peripheral Substitution: An Easy Way to Tuning the Magnetic Behavior of Tetrakis(phthalocyaninato) Dysprosium(III) SMMs

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Two tetrakis(phthalocyaninato) dysprosium(III)-cadmium(II) single-molecule magnets (SMMs) with different extent of phthalocyanine peripheral substitution and therefore different coordination geometry for the Dy ions were revealed to exhibit different SMM behavior, providing an easy way to tuning and controlling the molecular structure and in turn the magnetic properties of tetrakis(tetrapyrrole) lanthanide SMMs through simple tetrapyrrole peripheral substitution.

Results and Discussion

In the present paper, with the aim of tuning and controlling the molecular structure (actually the coordination geometry of the dysprosium spin carrier), two new tetrakis(phthalocyaninato) metal quadruple-decker complexes \{[Pc]Dy[Pc(OC₅H₁₁)₈]Cd[Pc(OC₅H₁₁)₈]Dy[Pc]\} (1) and \{[Pc]Dy[Pc(OC₅H₁₁)₈]Cd[Pc(OC₅H₁₁)₈]Dy[Pc(OC₅H₁₁)₈]\} (2) \{H₂Pc = unsubstituted phthalocyanine; H₂Pc(OC₅H₁₁)₈ = 2,3,9,10,16,17,23,24-octakis (pentyloxy)phthalocyanine\} with different extent of peripheral substitution for the phthalocyanine ligands have been designed and prepared from corresponding neutral bis(phthalocyaninato) dysprosium double-decker \{[Pc]Dy[Pc(OC₅H₁₁)₈]\} or \{[Pc]Dy[Pc(OC₅H₁₁)₈]\}, respectively. Figure 1. Single crystal X-ray diffraction analysis clearly reveals the different skew angle (defined as the rotation angle of one ring away from the eclipsed conformation of the two rings) for the bis(phthalocyaninato) dysprosium unit in these two quadruple-decker compounds. This in turn results in their obvious different SMM behavior according to magnetic mea-
surements, not only revealing the structure-magnetic property relationship but more importantly providing an easy but effective way towards effectively tuning the SMM behavior of tetrakis(phthalocyaninato) lanthanide quadruple-deckers through simple peripheral substitution.

On the basis of theoretical rationalization, tetrakis(phthalocyaninato) rare earth-cadmium complexes \([\text{Pc}(OC_{8}H_{17})_{8}]M[\text{Pc}(OC_{8}H_{17})_{8}]Cd[\text{Pc}(OC_{8}H_{17})_{8}]M[\text{Pc}(OC_{8}H_{17})_{8}]\) (M = Y, Pr-Yb except Pm) have been effectively synthesized and isolated quite recently through the solution instead of solid phase condensation pathway with neutral instead of reduced form of bis(phthalocyaninato) rare earth double-decker as starting material \(^{19–21}\). In the present case, both bis(phthalocyaninato) dysprosium double-decker compounds \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) (1) and \([\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]Cd[\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\) (2) with good yield of 73% and 61%. It is worth noting that when the heteroleptic bis(phthalocyaninato) dysprosium \([\text{Pc}M[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]M[\text{Pc}(OC_{5}H_{11})_{8}]\] was employed as starting material, only quadruple-decker with the conformation \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) (1) and \([\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]Cd[\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\) (2) was isolated without the detection of other possible quadruple-decker isomers according to the NMR spectroscopy \(^{23–25}\), due to the dominant electronic effect in the heteroleptic double-decker molecule of \([\text{Pc}M[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]M[\text{Pc}(OC_{5}H_{11})_{8}]\].

Figure S1 and S2 (Supplemental Information) show the \(^1H\) NMR and \(^1H-^1H\) COSY spectra of 1 and 2, respectively. Assignments of all the signals for both quadruple-decker compounds were easily achieved by virtue of the sets of chemical shift in the \(\text{Pc}(OC_{5}H_{11})_{8}\) ligand with the help of two dimensional \(^1H-^1H\) COSY spectra, Table S2 (Supplemental Information). It is worth noting that for the quadruple-decker \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) (1), the nonperipheral protons of the inner \(\text{Pc}(OC_{5}H_{11})_{8}\) rings give signal at \(\delta = 38.55\) ppm. Very interestingly, despite the replacement of the outer unsubstituted \(\text{Pc}\) rings by \(\text{Pc}(OC_{5}H_{11})_{8}\) in \([\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]Cd[\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\) (2), the nonperipheral protons of the inner \(\text{Pc}(OC_{5}H_{11})_{8}\) rings still resonate almost at the same position, \(\delta = 38.05\) ppm, revealing their same axial anisotropy \(^{26,27}\) and suggesting the almost same skew angle for the \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) subunit in 1 and \([\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]Cd[\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\) subunit in 2 in solution state.

Single crystals of both quadruple-decker compounds suitable for X-ray diffraction analysis were obtained by diffusing methanol into the solution of corresponding compound in \(\text{CHCl}_3\). Compound 1 crystallizes in the monoclinic system with a \(\text{C}2/c\), while 2 in the triclinic system with a \(P-1\) space group. The sandwich nature of both tetrakis(phthalocyaninato) dysprosium(III)-cadmium(II) compounds with symmetric quadruple-decker molecular structure was confirmed by single crystal X-ray diffraction analysis, Table S3 (Supplemental Information). As shown in Figure 2, each quadruple-decker molecule of 1 is composed of two \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) units connected by an intermediate \(\text{Cd}(\text{II})\) ion which is eight-coordinated by eight isoindole nitrogen atoms from two inner phthalocyanine ligands. The skew angle for the \([\text{Pc}Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy(\text{Pc})]\) subunit is 41.42° and the magic angle (defined as the angle between the \(S_8\) axis and a \(\text{Dy}-\text{N}\) direction) is 53.05°, Table S4 (Supplemental Information), revealing the almost ideal square-antiprismatic (SAP) polyhedron around the dysprosium ion (45° for the skew angle and 54.74° for the magic angle) \(^{28}\). The displacements of the dysprosium ion with respect to the four isoindole nitrogen atom mean planes are \(\text{Dy}-\text{N}_\text{a}(\text{Pc}) = 1.326\ \text{Å}\) and \(\text{Dy}-\text{N}_\text{a}(\text{Pc}) = 1.621\ \text{Å}\). As for the homoleptic analogue 2, the skew angle for the \([\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\text{Cd}[\text{Pc}(OC_{5}H_{11})_{8}]Dy[\text{Pc}(OC_{5}H_{11})_{8}]\) subunit decreases to 23.46°, resulting in a significantly distorted square antiprism coordination polyhedron around the dysprosium ion, while the magic angle is...
The displacements of the dysprosium ion with respect to the four isoindole nitrogen atom mean planes are Dy-N$_4$[Pc(OC$_5$H$_{11}$)$_8$] (outer) = 1.321 Å and Dy-N$_4$[P(cOC$_3$H$_{11}$)$_8$] (inner) = 1.681 Å, respectively.

The static magnetic properties of the two tetrakis(phthalocyaninato) dysprosium quadruple-deckers have been investigated. The temperature dependence of the magnetic susceptibility $\chi_M$ for 1 and 2 is shown in Figure S3 (Supplemental Information). The values of $\chi_M$ at 300 K are 28.32 for 1 and 28.04 cm$^3$/K mol$^{-1}$ for 2, respectively, both of which are close to 28.34 cm$^3$/K mol$^{-1}$ that is expected for two Dy(III) ions $[^4H_{15/2}, S = 5/2, L = 5, g = 4/3]^{29-31}$. When the temperature gets lowered, the $\chi_M$ values decrease slowly until about 60 K, then decrease quickly to a minimum value of 23.32 and 22.02 cm$^3$/K mol$^{-1}$ at 2 K. Such kind of magnetic behavior for both compounds should mainly originate from the crystal-field effect including thermal depopulation of the dysprosium(III) Stark sublevels and the presence of antiferromagnetic dipole-dipole interaction between the two adjacent double-decker subunits.

According to Curie-Weiss law, fitting the experimental data from 2 to 300 K gives the Curie constant ($C$, 28.38 and 28.74 cm$^3$/K mol$^{-1}$ for 1 and 2, respectively, and Weiss constant $\theta = -5.89$ (1) and $-6.56$ K (2). Such a fact that the field dependence magnetization $M$ ($H/T$) data at low temperature are far from the saturation magnetization value of 10 $\mu_B$ expected for even one Dy(III) ion ($J = 15/2, g = 4/3$), in combination with the non-superimposition character of the isothermal field dependence $M$ vs $H/T$ curves for 1 and 2, Figure S4 (Supplemental Information), discloses the presence of the crystal-field effect and the magnetic anisotropy for the Dy(III) ion in the quadruple-decker compounds, suggesting their potential SMM nature$^{35-38}$.

For the purpose to further reveal the magnetic relaxation of these compounds, the dynamics of magnetization was studied on multi-crystalline powder samples of 1 and 2 in a 3.0 Oe ac field oscillating at 1.0–780 Hz. Figure 3 displays the plots of $\chi'$ vs. $T$ $\chi''$ vs. $T$ in a zero dc field for 1 (A, B) and 2 (C, D). As can be seen, the frequency dependent in-phase ($\chi'$) and out-of-phase signals ($\chi''$) show the slow relaxation of magnetization for the two compounds, confirming their SMM nature. Nevertheless, for 1, the $\chi''$ signal starts to show clear frequency-dependent peak at the frequency as even low as 10 Hz, while 2 shows $\chi'$ peak at 320 Hz, revealing a faster relaxation due to the quantum tunneling of magnetization (QTM) than 1 because of the larger deviation of the coordination geometry for the Dy spin carriers from the ideal square antiprism molecular symmetry as indicated by the skew angle of 23.46$^\circ$ for 2, in comparison with the skew angle of 41.42$^\circ$ for 1. Based on a thermally activated mechanism, $\tau = \tau_0\exp(U_{\text{eff}}/kT)$ and $\tau = 1/(2\pi\nu)$, the Arrhenius law fitting for the picked peaks in the $\chi''$ vs $T$ curves in zero field for these two compounds was then carried out, revealing a linear relationship between ln($\tau$) and $1/T$ in the temperature range of 2.5–6.0 K for 1 and 2.5–3.2 K for 2. This in turn results in an energy barrier with $U_{\text{eff}} = 16.42$ cm$^{-1}$ (23.65 K) and pre-exponential factor $\tau_0 = 3.84 \times 10^{-15}$ s with $R = 0.996$ for 1, Figure S5 (Supplemental Information), and $U_{\text{eff}} = 12.00$ cm$^{-1}$ (17.28 K) and $\tau_0 = 8.83 \times 10^{-7}$ s with $R = 0.999$ for 2. Obviously, the energy barrier of 1 is larger than that of 2, revealing again the effect of the deviation of the coordination geometry for the dysprosium spin carriers from the ideal SAP polyhedron on the magnetic properties of sandwich-type quadruple-decker complexes$^{39}$. As detailed above, unlike in the solution state, 1 and 2 in the single crystal state possess two similar magic angle but significantly different skew angle for the (Pc$^{9}$/Dy(Pc$^{9}$) units, which then results in the different SAP environment. This in turn is responsible for the different energy barrier between these two compounds. Nevertheless, graphical representation of $\chi''$ vs $\nu$’ (Cole-Cole plot) at 2.0, 3.0, 5.0 K for both 1 and 2 give one semicircle, suggesting the existence of one magnetic relaxation processes, Figure S6 (Supplemental Information). Fitting of the experimental data according to the modified Debye function equation$^{39}$ gives the following sets of parameters with $\alpha = 0.19–0.29$ for 1 and $\alpha = 0.24–0.25$ for 2.

In addition, the dynamic susceptibility was also measured in a static magnetic field $H = 2000$ Oe to suppress the QTM for both compounds. As exhibited in Figure 4, very clear peak is observed in the $\chi''$ vs $T$ curves of 1 even at the frequency as low as 1.0 Hz, while the peaks for 2 are able to be observed only above relatively high frequency by 100 Hz. Anyway, these results indicate a typical slowing down of the relaxation mechanism. Nevertheless, the ac susceptibility data for these two compounds show an overall reduction in height due to the saturation effect. The corresponding Arrhenius law fitting for the $\chi''$ vs $T$ data under an external 2000 Oe field gives effective energy barrier $U_{\text{eff}} = 27.35$ cm$^{-1}$ (39.38 K) and $\tau_0 = 7.91$
In summary, two new sandwich-type tetrakis(phthalocyaninato) dysprosium complexes with different extent of peripheral substitution on the phthalocyanine ligands have been prepared and structurally characterized. Comparative studies in their magnetic properties reveal the close relationship between the coordination geometry of the dysprosium spin carrier and the SMM behavior. This result is surely helpful for the design and synthesis of novel sandwich-type tetrakis(tetrapyrrole) lanthanide SMMs with their molecular structure and in turn magnetic properties optimized through simple tetrpyrrole peripheral substitution.

Methods

General remarks. 1,2,4-Trichlorobenzene (TCB) and dichloromethane were freshly distilled from CaH₂ under nitrogen. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. All other reagents and solvents were used as received. The compounds of [{(Pc)Dy[OC₅H₁₁]₂}] and [{Pc(OC₅H₁₁)₈[Dy[Pc(OC₅H₁₁)₈,…}] were prepared according to the published procedure.

The synthesis of 1 and 2. A mixture of neutral bis(phthalocyaninato) dysprosium compound [{(Pc)Dy[OC₅H₁₁]₂}] (37.4 mg, 0.02 mmol) and Cd(OAc)₂.2H₂O (3.3 mg, 0.02 mmol) in TCB (2 ml) was heated to reflux under nitrogen for 3 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using CHCl₃ as the eluent to give a green band, which contained mainly the unreacted bis(phthalocyaninato) dysprosium double-decker [{(Pc)Dy[PC(OC₅H₁₁)₂]}]. Further elution with CHCl₃ gave a blue band containing the target quadruple-decker complex [{(Pc)Dy[PC(OC₅H₁₁)₂]Cd[PC(OC₅H₁₁)₂]Dy(Pc)} (1), 27.2 mg (73%). A similar manner with different double-decker as starting material, isolation of 2 in the yield of 61% was also achieved.

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Author contributions

H.S., H.W. and J.J. designed the experiments and wrote the main paper; S.Z. and J.D. performed the magnetic measurements. All authors reviewed the manuscript.

Additional information

Accession codes: CCDC 926978 for 1 and CCDC 994848 for 2 contains 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.

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