

# Structures and Magnetic Properties of Two Analogous Dy<sub>6</sub> Wheels with Electron-Donation and -Withdrawal Effects

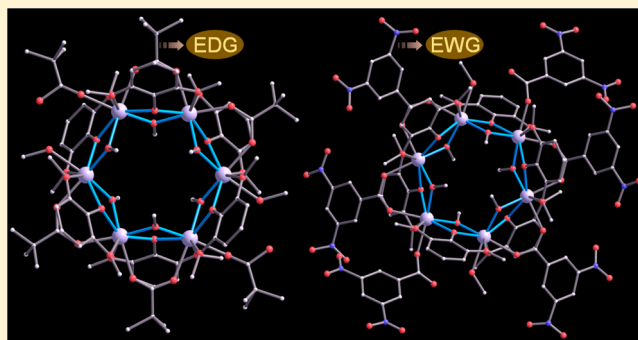
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**S** Supporting Information

**ABSTRACT:** Two new hexanuclear symmetric dysprosium wheels, namely, [Dy<sub>6</sub>(L<sub>1</sub>)<sub>6</sub>(L')<sub>6</sub>(OCH<sub>3</sub>)<sub>6</sub>(2CH<sub>3</sub>OH)] and [Dy<sub>6</sub>(L<sub>2</sub>)<sub>6</sub>(L')<sub>6</sub>(OCH<sub>3</sub>)<sub>6</sub>(2CH<sub>3</sub>OH)] (L<sub>1</sub>H = pivalic acid and L<sub>2</sub>H = 3,5-dinitrobenzoic acid, L'H = 2,6-dimethoxyphenol) were isolated employing a mixed-ligand strategy. The strategic introduction of two different auxiliary groups with diverse steric effects and electrostatic actions affect the magnetic coupling and local anisotropy of Dy<sup>III</sup> ion, therefore exhibiting dissimilar magnetic behaviors.



## INTRODUCTION

The seminal discovery of single molecule magnet (SMM) behavior<sup>1,2</sup> in dodecanuclear mixed-valent manganese (III/IV) cluster<sup>3</sup> triggered the persistent drive right through the past decade, to develop novel molecular magnets aimed to miniaturize devices in the nanoregime involving high-density information storage, quantum computing, and molecule spintronics.<sup>4</sup> SMMs are molecular species typically characterized by the slow relaxation of the magnetization due to the unique combination of both high-spin (*S*) ground state and uniaxial (negative) magnetic anisotropy (*D*), leading to an anisotropy energy barrier (*U*) for the concomitant reversal of magnetization vector  $S^2|D|$ .<sup>5</sup> After the initial extensive study on polynuclear 3d metal aggregates, especially large manganese complexes, was carried out as a prime focus by chemists, physicists, and material scientists,<sup>6</sup> recent years have particularly seen a flurry of interesting results out of lanthanide-based SMMs,<sup>7</sup> including the achievement of maximum relaxation energy barriers<sup>8</sup> for multinuclear clusters and the highest blocking temperature.<sup>9</sup> This promising strategy to design novel homometallic lanthanide-based SMMs solely benefit from the significant magnetic anisotropy of lanthanide ions such as Dy<sup>III</sup> owing to their inherently large, unquenched orbital angular momentum.<sup>10</sup> Since the SMM behavior has been established to be directed by the crucial interplay of the ligand field effect, coordination geometry, and the strength of the magnetic interactions between the neighboring lanthanide sites, the design of coordination chemistry assemblies represents a key avenue for accessing tailor-made functional SMMs.<sup>11</sup>

Whereas the energy barriers (giving rise to magnetic bistability and slow magnetization relaxation) have been

following a trend of steady escalation with diverse-natured 48 novel molecular clusters, a more systematic approach is 49 essentially required to elucidate the origin of slow relaxation 50 as well as target rational methods of synthesizing better SMMs. 51 This led to the mixed-ligand based strategy<sup>12</sup> to synthesize two 52 analogous dysprosium-based SMMs, differing only in the nature 53 of the respective coordinated carboxylic acid ligands. As a point 54 of reference, very recently the effects of electron-withdrawing 55 substituents on the energy barrier-enhancement for five novel 56 Dy<sub>2</sub> SMMs has been shown as the first report of a direct 57 correlation between relaxation barriers and electron-with- 58 drawing groups on terminal ligands while retaining the 59 geometry of the lanthanide ions intact.<sup>13</sup> 60

Herein, we report two dysprosium-based symmetric 61 hexanuclear wheel compounds (Dy<sub>6</sub>), namely, 62 [Dy<sub>6</sub>(L<sub>1</sub>)<sub>6</sub>(L')<sub>6</sub>(OCH<sub>3</sub>)<sub>6</sub>(2CH<sub>3</sub>OH)] (1) and 63 [Dy<sub>6</sub>(L<sub>2</sub>)<sub>6</sub>(L')<sub>6</sub>(OCH<sub>3</sub>)<sub>6</sub>(2CH<sub>3</sub>OH)] (2) (L<sub>1</sub>H = pivalic acid, 64 L<sub>2</sub>H = 3,5-dinitrobenzoic acid, and L'H = 2,6-dimethoxyphenol) 65 by the designed variation principle of the participating 66 carboxylic acid ligands (Figure 1), aimed to study the 67 differential effects of the opposite-natured ligands on the 68 SMM property for these two analogous molecular magnets. 69

The electron-rich pivalic acid (L<sub>1</sub>H) ligands are expected to 70 make the central wheel electron-rich owing to +I effects of the 71 three methyl groups; as a parallel event, the highly electron- 72 withdrawing -R effect of nitro groups in the analogous ligand 73 3,5-dinitrobenzoic acid leaves the other Dy<sub>6</sub> wheel somewhat 74 electron-deficient. This differential nature of electron-density of 75

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