

Cite this: *Chem. Sci.*, 2025, 16, 21404

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# Chiral tether-guided selective synthesis of $D_n$ -symmetric chiral conjugated nanorings

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Chiral conjugated nanorings with  $D_n$  symmetry exhibit extraordinary circularly polarized luminescence (CPL) properties due to their unique cylindrical helical conjugated system. However, their synthesis faces challenges such as numerous atropisomers and tedious separation and chiral resolution processes, which severely hinder their development. In this work, we report a chiral tether-guided synthesis strategy. By introducing a strained planar chiral alkyl chain tether into the fused-ring building unit of the nanoring, the energy differences between the various atropisomers of the nanoring are significantly increased. This guides the formation of the thermodynamically most stable  $D_n$ -symmetric isomer during synthesis, thus greatly enhancing the selectivity. Four chiral nanorings,  $D_3$ -(P)-NR1,  $D_4$ -(P)-NR1,  $D_3$ -(M)-NR2, and  $D_4$ -(M)-NR2, as well as their enantiomers, were facily obtained through this method. All molecules have shown remarkable and stable CPL capability, with a luminescence dissymmetry factor up to 0.076.

Received 22nd August 2025  
Accepted 9th October 2025

DOI: 10.1039/d5sc06445g

rsc.li/chemical-science

## Introduction

In recent years, organic luminescent materials have achieved widespread applications in fields such as electroluminescence, biological probes, information encryption, sensing and detection.<sup>1–7</sup> Chirality further endows them with circularly polarized luminescence (CPL) properties, significantly expanding their application potential and making them highly promising for 3D displays, optical storage, polarized imaging, chiral sensing, and spintronics.<sup>8–15</sup> Two key metrics for evaluating the performance of chiral luminescent materials are the photoluminescence quantum yield ( $\phi$ ) and the luminescence dissymmetry factor ( $g_{\text{lum}}$ ). For organic luminescent molecules, the  $\phi$  can reach 100% through molecular design and excited-state modulation. However, the intrinsic  $g_{\text{lum}}$  values of most organic chiral molecules typically fall within the range of  $10^{-5}$

to  $10^{-3}$ ,<sup>16</sup> far below the theoretical extremes ( $\pm 2$ ). Developing organic chiral molecules with intrinsically large  $g_{\text{lum}}$  values holds significant scientific importance.

Theoretically, the  $g_{\text{lum}}$  of chiral luminescent molecules can be described by the following equation:

$$g = \frac{4|\mu_{ij}||m_{ij}|\cos\theta}{|\mu_{ij}|^2 + |m_{ij}|^2}$$

where  $\mu_{ij}$  and  $m_{ij}$  represent the electric transition dipole moment and magnetic transition dipole moment, respectively, during the transition from excited state ' $i$ ' to ground state ' $j$ ', and  $\theta$  is the angle between the two transition dipole moments.<sup>17,18</sup> Since the luminescence of most organic molecules follows Kasha's rule, the transition of interest is typically from the  $S_1$  to  $S_0$  state.<sup>19</sup> The equation indicates that to maximize the  $g$  value while maintaining high luminescence intensity, both  $\mu$  and  $m$  must be large and comparable in magnitude, while their dipole moments must be aligned parallel or antiparallel (i.e.,  $\theta = 0$  or  $180$ ). However, for most organic chiral molecules,  $m$  is much smaller than  $\mu$ , making it difficult to enhance  $g_{\text{lum}}$ .<sup>20</sup> Therefore, the key to improving  $g_{\text{lum}}$  lies in molecular design strategies that enhance  $m$  while ensuring  $\mu$  and  $m$  remain parallel or antiparallel. In recent years, significant efforts have been devoted to exploring chiral organic luminescent molecules with high  $g_{\text{lum}}$  values.<sup>21–47</sup> Among all reported chiral organic emitters, conjugated nanorings with  $D_n$  symmetry exhibit exceptionally high intrinsic  $g_{\text{lum}}$ . For example, Isobe's  $D_4$ -symmetric (P)-(12,8)-[4]CC<sup>45</sup> and Du's  $D_4$ -symmetric (+)-[4]CAN<sub>2,6</sub> ref. 46 achieved  $|g_{\text{lum}}|$  of 0.152 and 0.103,

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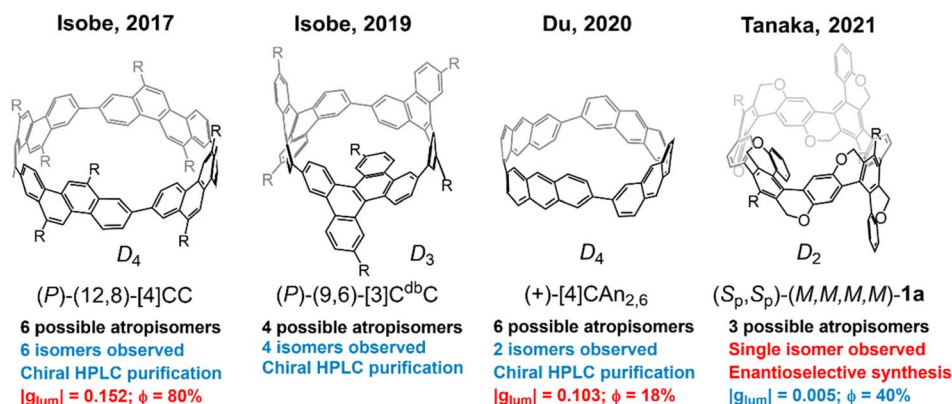
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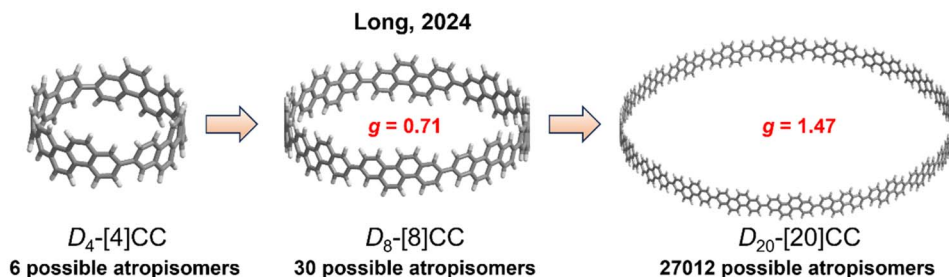
respectively (Fig. 1a), representing the only two purely organic chiral emitters with  $|g_{lum}|$  on the order of  $10^{-1}$  at the molecular level. Notably, (*P*)-(12,8)-[4]CC also exhibited a high fluorescence quantum yield of 80%. The extraordinary  $|g_{lum}|$  in these molecules arises from their unique cylindrical helical conjugated systems. On one hand, this structure arranges the local electric transition dipole moments of the building units in

a circular fashion, generating a large induced magnetic transition dipole moment along the helical axis.<sup>48</sup> On the other hand, their high  $D_n$  symmetry ensures that  $\mu$  and  $m$  remain parallel or antiparallel, maximizing  $|\cos \theta|$  and thus achieving a large  $|g_{lum}|$ .<sup>44,49</sup> Long *et al.* further demonstrated through theoretical calculations that increasing the number of building units to synthesize higher-order  $D_n$ -symmetric nanorings could

(a) Previously reported  $D_n$ -symmetric chiral conjugated nanorings:



(b) Theoretically predicted high-order  $D_n$ -nanorings with giant  $g$ -values:



(c) This work: chiral tether-guided selective synthesis of  $D_n$ -nanorings

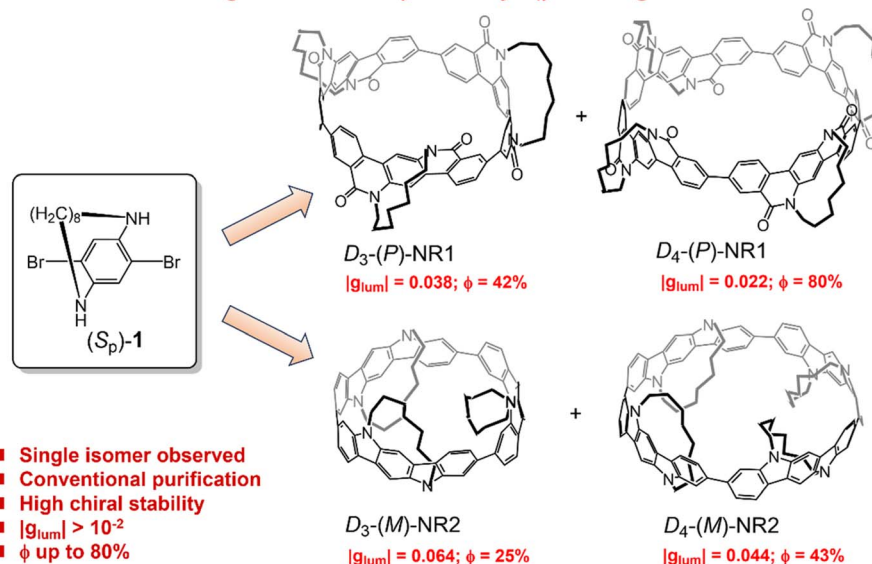


Fig. 1 (a) Previously reported  $D_n$ -symmetric chiral conjugated nanorings. (b) Theoretically predicted high-order  $D_n$ -nanorings with giant  $g$ -values. (c) Chiral tether-guided selective synthesis of  $D_n$ -nanorings in this work.



significantly enhance the magnetic transition dipole moment along the helical axis, enabling giant  $g$  values (Fig. 1b).<sup>50</sup> For instance, starting from Isobe's [4]CC framework, expanding to a  $D_8$ -symmetric [8]CC (8 units) increases  $g$  to 0.71, while a  $D_{20}$ -symmetric [20]CC (20 units) could further elevate  $g$  to 1.47, all while maintaining high transition oscillator strengths.

The above experimental and theoretical studies demonstrate that  $D_n$ -symmetric chiral conjugated nanorings represent a highly promising class of molecules, offering potential breakthroughs in organic luminescent materials with intrinsically giant  $g_{lum}$  values. However, their synthesis faces a critical challenge: the formation of atropisomers (conformational isomers arising from flipping of building units) during preparation. The number of atropisomers increases rapidly with higher symmetry order ( $n$ ). Tanaka *et al.* reported a  $D_2$ -symmetric nanoring ( $S_p, S_p$ )-(M,M,M,M)-1a, which theoretically has 3 atropisomers (Fig. 1a). While an asymmetric catalytic cyclization enabled the selective synthesis of the  $D_2$ -symmetric isomer, its  $|g_{lum}|$  was only 0.005.<sup>51</sup> Isobe *et al.* observed all 4 possible atropisomers in the preparation of  $D_3$ -symmetric nanoring (P)-(9,6)-[3]C<sup>db</sup>C. The optically pure (P)-(9,6)-[3]C<sup>db</sup>C was obtained *via* chiral HPLC purification.<sup>48</sup> For  $D_4$ -symmetric nanorings, the number of atropisomers rises to 6. Aforementioned (P)-(12,8)-[4]CC and (+)-[4]CAN<sub>2,6</sub> both required laborious chiral HPLC purification.<sup>45,46</sup> For higher-order systems like  $D_8$ -symmetric [8]CC and  $D_{20}$ -symmetric [20]CC proposed by Long *et al.*, the atropisomer count escalates to 30 and 27012, respectively, making their synthesis and isolation extremely challenging.<sup>50</sup> Thus, developing a method to selectively access  $D_n$ -symmetric nanorings is crucial to advance their applications in chiral organic luminescent materials. In this work, we report a novel chiral tether-guided synthesis strategy for  $D_n$ -symmetric chiral conjugated nanorings (Fig. 1c). By incorporating a strained planar-chiral alkyl tether into the fused-ring building block of the nanoring, we significantly amplify the energy differences between various atropisomers. This thermodynamic control drives the formation of the most stable  $D_n$ -symmetric isomer with exceptional selectivity during synthesis. Using this innovative approach, we successfully synthesized four chiral nanorings:  $D_3$ -(P)-NR1,  $D_4$ -(P)-NR1,  $D_3$ -(M)-NR2, and  $D_4$ -(M)-NR2, along with their respective enantiomers. The helical chirality of these molecules is uniquely determined by the planar chirality of their tether moieties. These compounds exhibit remarkable CPL properties, with all derivatives demonstrating  $|g_{lum}|$  exceeding  $10^{-2}$ .

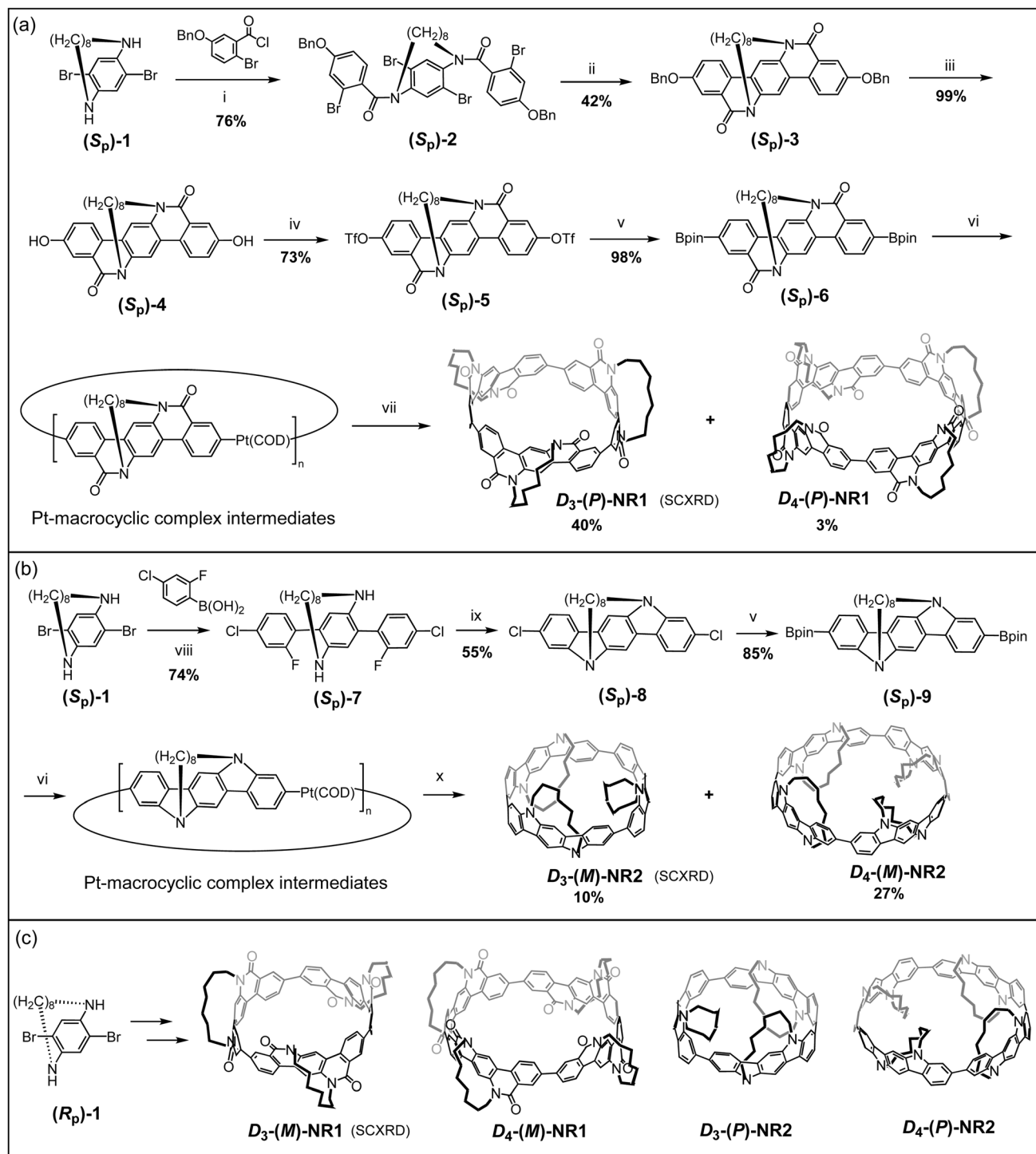
## Results and discussion

The synthetic routes for the nanorings are illustrated in Scheme 1. For  $D_3$ -(P)-NR1 and  $D_4$ -(P)-NR1 (Scheme 1a), starting from the previously reported planar chiral cyclophane ( $S_p$ )-1,<sup>52</sup> the synthesis proceeded *via* acylation to afford the dibenzoyloxy-terminated amide ( $S_p$ )-2. Subsequent intramolecular Yamamoto cyclization yielded the pentacyclic fused lactam ( $S_p$ )-3.<sup>53–55</sup> Deprotection of the benzyl groups followed by acylation furnished the triflate-terminated intermediate ( $S_p$ )-5, which was further converted into the boronic ester ( $S_p$ )-6 *via* Pd-catalyzed

borylation. Equimolar reaction of ( $S_p$ )-6 with Pt(COD)Cl<sub>2</sub> generated the Pt-macrocyclic complex intermediates, and final reductive elimination promoted by PPh<sub>3</sub> afforded the chiral trimeric ring  $D_3$ -(P)-NR1 and the chiral tetrameric ring  $D_4$ -(P)-NR1 in yields of 40% and 3% (starting from ( $S_p$ )-6), respectively. The preferential formation of the trimer suggests that the highly curved backbone of the fused-ring unit ( $S_p$ )-6 favors smaller macrocycles in this Pt-mediated nanoring synthesis.<sup>48</sup> For  $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2 (Scheme 1b), ( $S_p$ )-1 first underwent Suzuki coupling with 3-chloro-2-fluorobenzeneboronic acid to afford ( $S_p$ )-7, which was cyclized *via* a potassium *tert*-butoxide-mediated intramolecular nucleophilic substitution to form the pentacyclic carbazole ( $S_p$ )-8.<sup>52,56</sup> Pd-catalyzed borylation then replaced the terminal chlorine with a boronic ester, yielding ( $S_p$ )-9. Subsequent Pt-mediated macrocyclization produced the chiral trimer  $D_3$ -(M)-NR2 and the chiral tetramer  $D_4$ -(M)-NR2 in 10% and 27% yields (starting from ( $S_p$ )-9), respectively. Unlike the fused-lactam-based system, the fused-carbazole-derived nanoring predominantly formed the tetrameric product. Using the enantiomeric planar chiral cyclophane ( $R_p$ )-1 as the starting material, we also synthesized the enantiomers of the above four nanorings— $D_3$ -(M)-NR1,  $D_4$ -(M)-NR1,  $D_3$ -(P)-NR2 and  $D_4$ -(P)-NR2 (Scheme 1c). Detailed synthetic procedures are provided in the SI (Schemes S3 and S4). It is worth mentioning that all the nanorings were obtained through conventional column chromatography separation, without the need for chiral HPLC purification. All nanoring structures were characterized by NMR and mass spectroscopic methods. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra confirmed that each nanoring was obtained as a single isomer (see SI). Additionally, single-crystal X-ray diffraction (SCXRD) analysis unambiguously determined the structures of  $D_3$ -(P)-NR1,  $D_3$ -(M)-NR2, and the enantiomer  $D_3$ -(M)-NR1 (*vide infra*).

The single-crystal structures of  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2 are shown in Fig. 2a, and that for  $D_3$ -(M)-NR1 is presented in Fig. S64. Crystallographic data reveal that all molecules adopt a single configuration without other atropisomers, and their ring skeletons exhibit  $D_3$  symmetry. Although both  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2 were synthesized from the same starting material, ( $S_p$ )-1, their macrocyclic structures differ significantly. In  $D_3$ -(P)-NR1, all the tethers are positioned on the outer periphery of the nanoring, and the three fused-ring lactam building blocks ( $S_p$ )-M1 adopt a clockwise *P*-helical arrangement. In contrast, in  $D_3$ -(M)-NR2, all the tethers are oriented inside the nanoring, and the three fused-ring carbazole units ( $S_p$ )-M2 form a counterclockwise *M*-helical arrangement.  $D_3$ -(M)-NR1, synthesized from ( $R_p$ )-1, shows the mirror-image structure of  $D_3$ -(P)-NR1, exhibiting *M*-helicity (Fig. S64). From the top view (Fig. 2b), the diameter of the lactam nanoring  $D_3$ -(P)-NR1 is larger (~12.7 Å), whereas that of the carbazole nanoring  $D_3$ -(M)-NR2 is slightly smaller (~12.1 Å). Regarding packing structures,  $D_3$ -(P)-NR1 molecules form a 2D layered arrangement, where adjacent nanorings within each layer are nearly perpendicular, resembling a herringbone pattern—similar to some known cycloparaphenylene (CPP) nanorings (*e.g.*, [6]CPP, [7]CPP).<sup>57,58</sup> In contrast,  $D_3$ -(M)-NR2 crystals exhibit a triangular packing motif: three nanoring molecules assemble into a circular





**Scheme 1** Synthetic routes for (a) *D*<sub>3</sub>-(P)-NR1 and *D*<sub>4</sub>-(P)-NR1, (b) *D*<sub>3</sub>-(M)-NR2 and *D*<sub>4</sub>-(M)-NR2, and (c) the enantiomers. Reaction conditions: (i) Et<sub>3</sub>N, 70 °C; (ii) Ni(COD)<sub>2</sub>/2,2'-bipyridine, 70 °C; (iii) Pd/C, NH<sub>4</sub>OOCH, 80 °C; (iv) Tf<sub>2</sub>O/pyridine; (v) (Bpin)<sub>2</sub>, Pd(OAc)<sub>2</sub>/S-Phos, 80 °C; (vi) (COD) PtCl<sub>2</sub>, CsF; (vii) PPh<sub>3</sub>, 110 °C; (viii) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, 70 °C; (ix) <sup>t</sup>BuOK, 80 °C; (x) PPh<sub>3</sub>, 150 °C.

trimer, with disordered solvent molecules filling the triangular pores. This arrangement resembles the triangular stacking observed in Itami's previously reported carbon nanobelts (CNB) (*e.g.*, [24]CNB).<sup>55</sup> To understand why *D*<sub>3</sub>-(P)-NR1 has all tethers outward while *D*<sub>3</sub>-(M)-NR2 has them inward, we examined the conformations of their building blocks, (*S*<sub>p</sub>)-M1 and (*S*<sub>p</sub>)-M2

(Fig. 2c). DFT-optimized structures show that the fused-ring backbone of (*S*<sub>p</sub>)-M1 bends outward due to tether-induced strain, favoring an exterior tether placement, whereas (*S*<sub>p</sub>)-M2 bends inward under the strain, directing its tethers inside the nanoring.



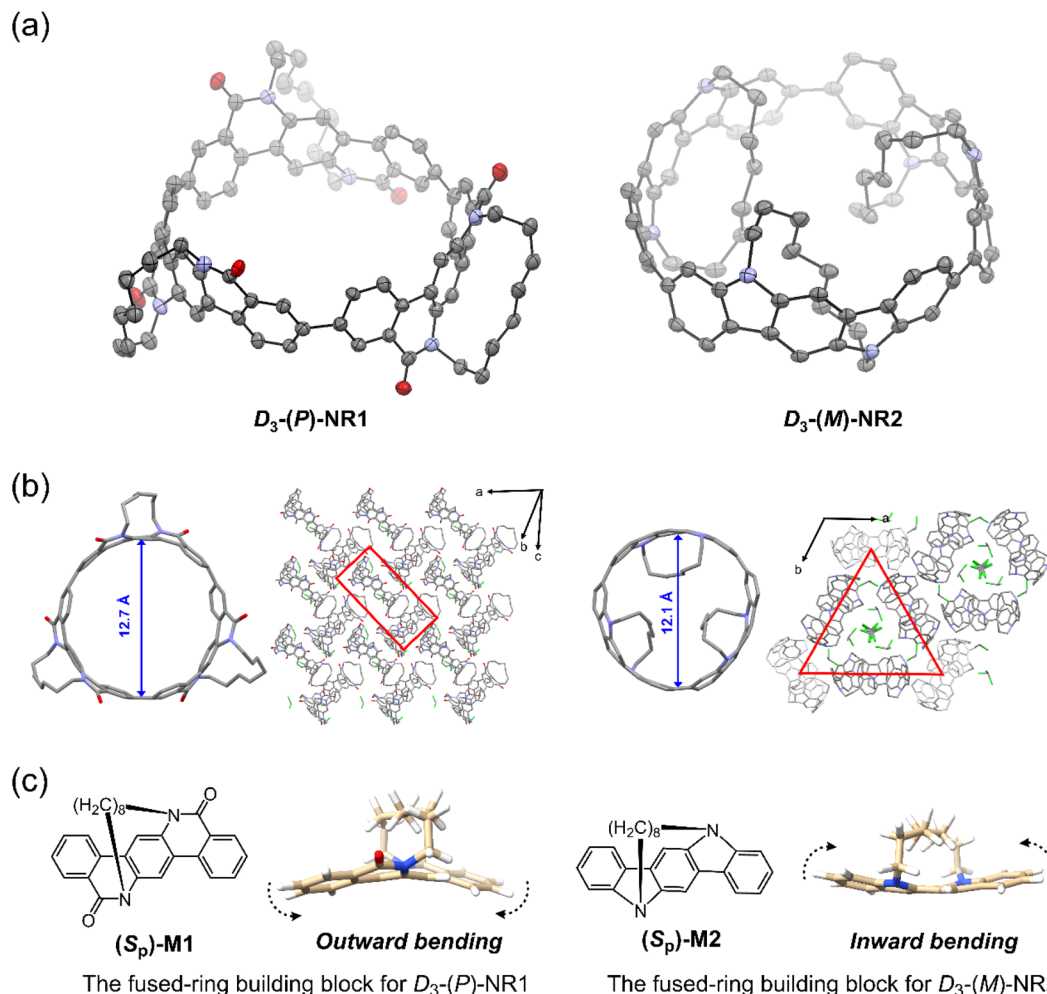


Fig. 2 (a) Single crystal structures for  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2; (b) top view and packing structures for  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2; (c) the fused-ring building blocks ( $S_p$ )-M1 and ( $S_p$ )-M2, and their DFT-optimized configurations. Note: the solvent systems used for single-crystal growth are hexane/dichloromethane and methanol/chloroform for  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2, respectively; the solvent molecules in the crystals of  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2 are dichloromethane and chloroform, respectively.

To elucidate the high selectivity in obtaining  $D_n$ -symmetric nanorings without observable formation of other atropisomeric products, we calculated the energies of all possible atropisomers. For comparison, we also calculated the energies of hypothetical tether-free nanorings (where one alkyl tether is replaced by two methyl groups). Fig. 3 shows the relative Gibbs free energies of all four possible atropisomers for the  $D_3$ -symmetric nanorings ( $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2) and their tether-free analogues. For  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR2, the lowest-energy isomers are *Aooo* and *Biii* ('o' (outside) and 'i' (inside) describe the tether's position with respect to the nanoring), respectively. These structures match the single-crystal configurations. Flipping one fused-ring unit to form *Aooi* and *Biio* raises the energy by 8.4 kcal mol<sup>-1</sup> and 24.6 kcal mol<sup>-1</sup>, respectively. Obviously, the  $D_3$ -symmetric *Aooo* and *Biii* are much favored energetically over other isomers. On the other hand, the tether-free analogues exhibit low energy differences (a few kcal mol<sup>-1</sup>) among atropisomers ('a' and 'b' denote the *syn*-facial and *anti*-facial arrangement of the fused-

ring building units) (Fig. 3c and d), consistent with prior reports.<sup>59</sup> Similar energies imply the lack of a dominant product, as all are likely to form during the synthesis. The above results indicate that by introducing strained chiral tethers into the nanoring significantly increases the energy differences among atropisomers, thereby enabling one  $D_n$ -symmetric isomer to become the dominant product and greatly enhancing selectivity. We also conducted energy analyses on all atropisomers of the  $D_4$ -symmetric nanorings  $D_4$ -(P)-NR1,  $D_4$ -(M)-NR2, and their tether-free analogues, arriving at the same conclusion (Fig. S65 and S66). Notably, the tether does not significantly affect the rotational barriers between the atropisomers. Similar to the tether-free nanorings,  $D_3$ -(P)-NR1,  $D_3$ -(M)-NR2,  $D_4$ -(P)-NR1, and  $D_4$ -(M)-NR2 all exhibit high atropisomerization barriers (21.4–67.5 kcal mol<sup>-1</sup>), indicating that they can maintain stable helical configurations with high chiral stability (Fig. S65 and S66).

The striking structural difference between the fused-lactam nanorings ( $D_3$ -(P)-NR1 and  $D_4$ -(P)-NR1) and fused-carbazole

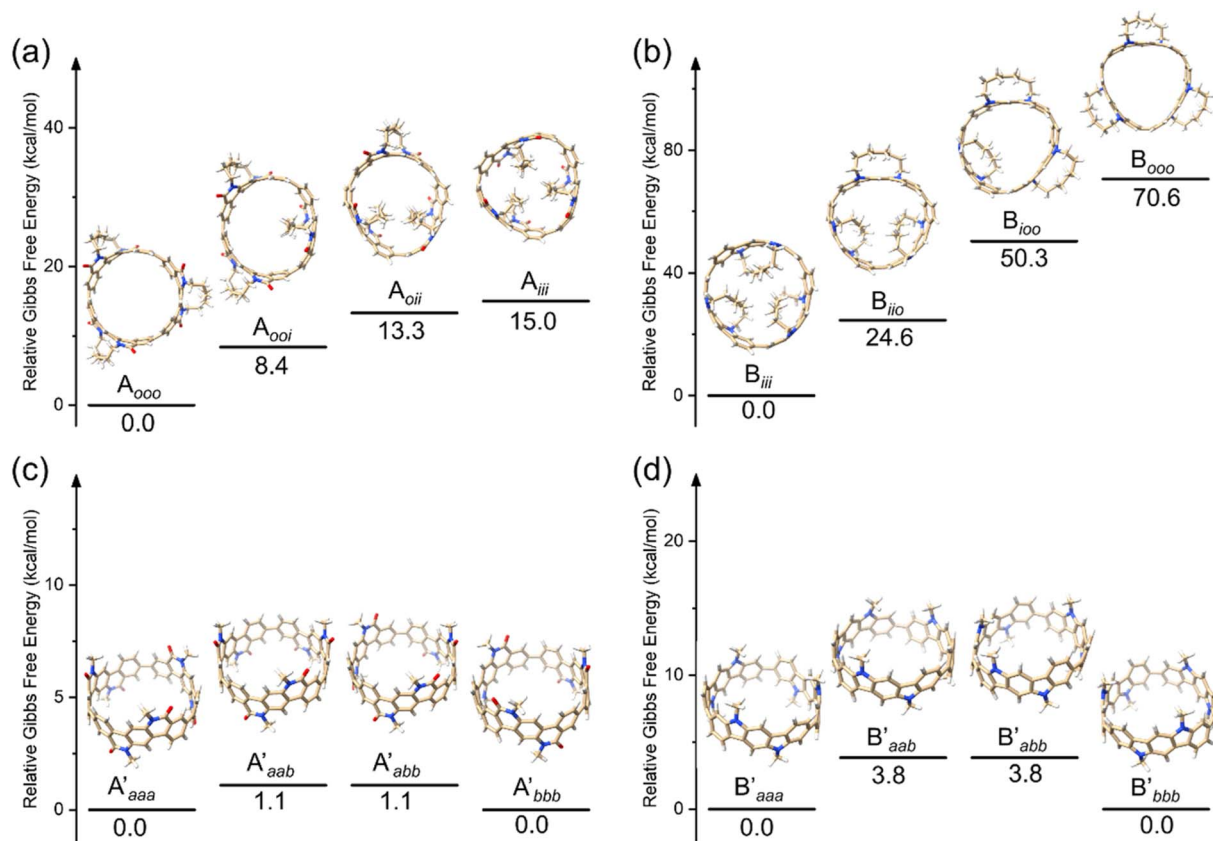


Fig. 3 The relative Gibbs free energies for different atropisomers of (a)  $D_3$ -(P)-NR1 (A series), (b)  $D_3$ -(M)-NR2 (B series) and the tether-free analogues of (c)  $D_3$ -(P)-NR1 (A' series) and (d)  $D_3$ -(M)-NR2 (B' series).

nanorings ( $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2), where the tethers are positioned exteriorly and interiorly respectively, results in significantly distinct chemical shifts of the tether protons in NMR spectra. Particularly, the most pronounced shift is observed for proton  $H_1$ , which is closest to the central benzene ring of the building block (Fig. 4a). For the fused-lactam building unit ( $S_p$ )-M1, its  $H_1$  appears at  $-0.29$  ppm due to its location above the central benzene ring, where it experiences shielding effects and resonates in a relatively upfield region. However, upon incorporation into nanorings  $D_3$ -(P)-NR1 and  $D_4$ -(P)-NR1, the chemical shift of  $H_1$  moves to 0.68 ppm and 0.57 ppm respectively, indicating markedly reduced shielding in the exterior regions of the nanorings. Conversely, for the fused-carbazole building unit ( $S_p$ )-M2,  $H_1$  initially appears at  $-1.86$  ppm. After being integrated into nanorings  $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2, its chemical shift moves to  $-3.90$  ppm and  $-3.11$  ppm, respectively, demonstrating enhanced shielding within the interior cavity of the nanorings. These experimental observations align well with the trends predicted by DFT calculations. Previous theoretical studies have proposed that the exterior and interior of certain cyclic nanocarbons correspond to less-shielded and shielded regions, respectively.<sup>60</sup> In this study,  $H_1$  worked as an NMR probe, providing direct experimental evidence. To further investigate the magnetic shielding environments, we computed the nucleus-independent chemical shift (NICS)<sup>61–63</sup> of the central benzene

rings (Fig. 4b). The results reveal that for all nanorings, the NICS(–1) values (interior) are consistently more negative than the NICS(1) values (exterior), confirming stronger shielding inside the rings, in agreement with our NMR observations. Moreover, compared to the building blocks, all nanorings exhibit less negative NICS(1) values, while the NICS(–1) values tend to become more negative (except for  $D_4$ -(M)-NR2, which shows minimal change). This suggests that upon nanoring formation, the increased curvature of the building units leads to reduced shielding on the convex side (exterior) and enhanced shielding on the concave side (interior), consistent with prior literature reports.<sup>64,65</sup> The average values (NICS<sub>avg</sub>) of NICS(1) and NICS(–1) show a clear trend toward less negative values from monomers to nanorings, indicating reduced aromaticity of the central benzene ring due to heightened curvature in the nanoring structures.

Next, we investigated the optical properties of the nanorings. Fig. 5a displays the UV-Vis absorption spectra of  $D_3$ -(P)-NR1,  $D_4$ -(P)-NR1,  $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2. Their respective enantiomers,  $D_3$ -(M)-NR1,  $D_4$ -(M)-NR1,  $D_3$ -(P)-NR2 and  $D_4$ -(P)-NR2, show identical spectra (Fig. S67). It can be observed that the spectra of the fused-lactam nanorings  $D_3$ -(P)-NR1 and  $D_4$ -(P)-NR1 primarily exhibit two absorption bands (one at 320–400 nm and another at 400–500 nm), whereas the fused-carbazole nanorings  $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2 show only one main absorption band at 320–420 nm. This difference is mainly attributed to the

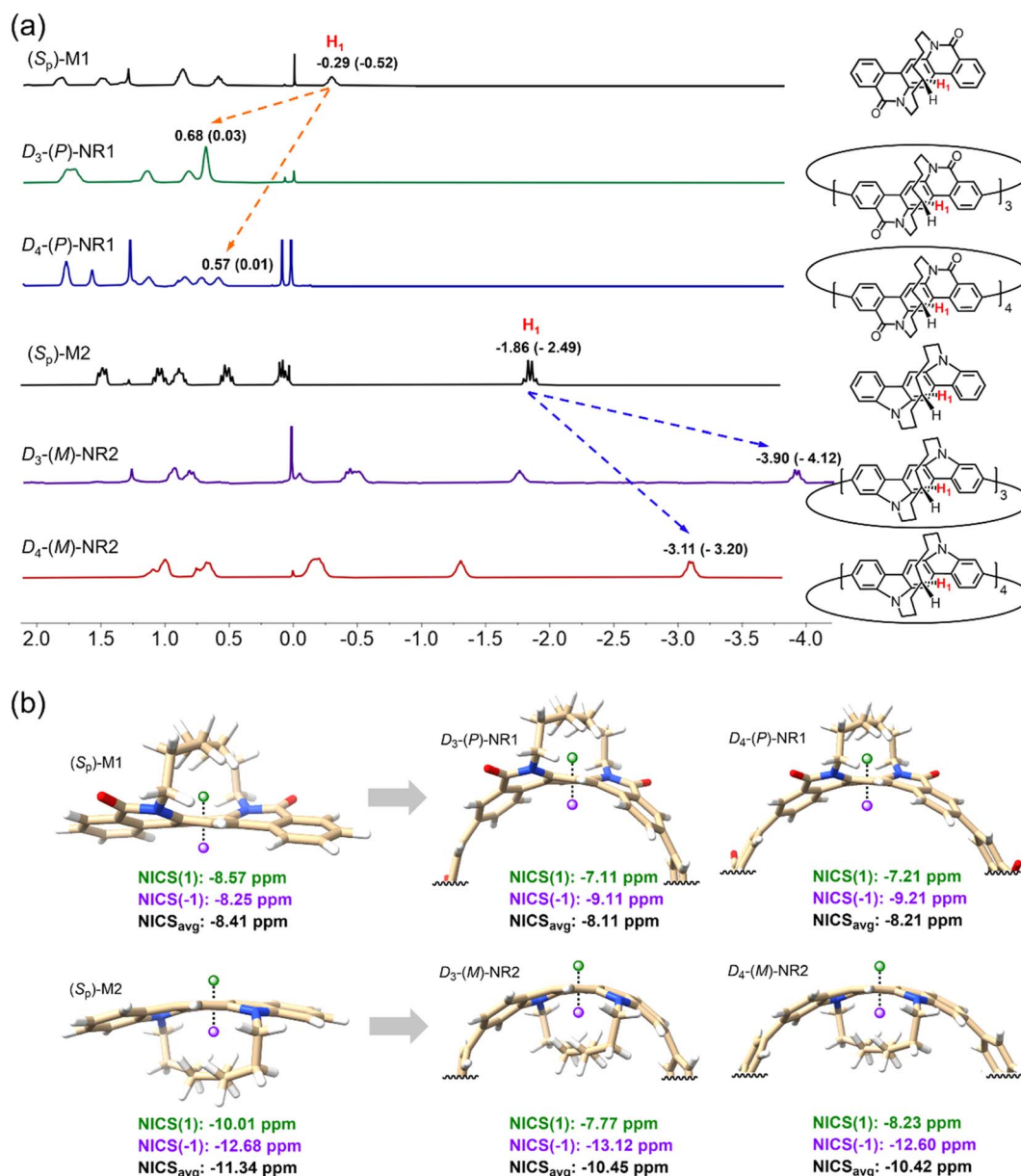


Fig. 4 (a) The change of the NMR chemical shifts (the values in parentheses are DFT-calculated chemical shifts) of proton H<sub>1</sub> from building blocks to nanorings; (b) the calculated NICS(1), NICS(−1) and the averages of NICS(1) and NICS(−1) for the building blocks and nanorings.

fact that some lower-energy electronic transitions (*e.g.*, S<sub>0</sub> → S<sub>2</sub>, S<sub>0</sub> → S<sub>3</sub>) in the fused-lactam nanorings exhibit higher oscillator strengths (Table S1). The oscillator strengths of the S<sub>0</sub> → S<sub>1</sub> transitions are very low for all nanorings, likely due to the high molecular symmetry, which makes the S<sub>0</sub> → S<sub>1</sub> transition forbidden. Consequently, the absorption coefficients near the bandgap are relatively low for all nanorings. From the onset absorption, the optical bandgaps of D<sub>3</sub>-(P)-NR1, D<sub>4</sub>-(P)-NR1, D<sub>3</sub>-(M)-NR2 and D<sub>4</sub>-(M)-NR2 are calculated to be 2.40, 2.51, 2.54, and 2.62 eV, respectively. It is evident that, for both fused-lactam and fused-carbazole nanorings, the smaller-sized nanorings possess narrower bandgaps than their larger-sized counterparts, consistent with previously reported trends for CPP and CNB nanorings.<sup>22,55,66</sup> DFT calculations further confirm

this observation, showing that smaller-sized nanorings have smaller HOMO–LUMO gaps (Fig. S69). Additionally, theoretical calculations indicate that the fused-carbazole nanorings have higher HOMO and LUMO energy levels compared to the fused-lactam nanorings, which aligns with the energy levels measured in electrochemical experiments (Fig. S70). The photoluminescence spectra of all nanorings and their enantiomers are shown in Fig. 5b and S71, respectively. All samples were measured in toluene solution. The excitation wavelengths were set at 360 nm for D<sub>3</sub>-(P/M)-NR1, 370 nm for D<sub>4</sub>-(P/M)-NR1, and 380 nm for both D<sub>3</sub>-(M/P)-NR2 and D<sub>4</sub>-(M/P)-NR2. The fluorescence peaks of D<sub>3</sub>-(P)-NR1, D<sub>4</sub>-(P)-NR1, D<sub>3</sub>-(M)-NR2 and D<sub>4</sub>-(M)-NR2 are located at 561, 520, 519, and 492 nm, respectively. The measured fluorescence quantum yields are 42%, 80%, 25%, and

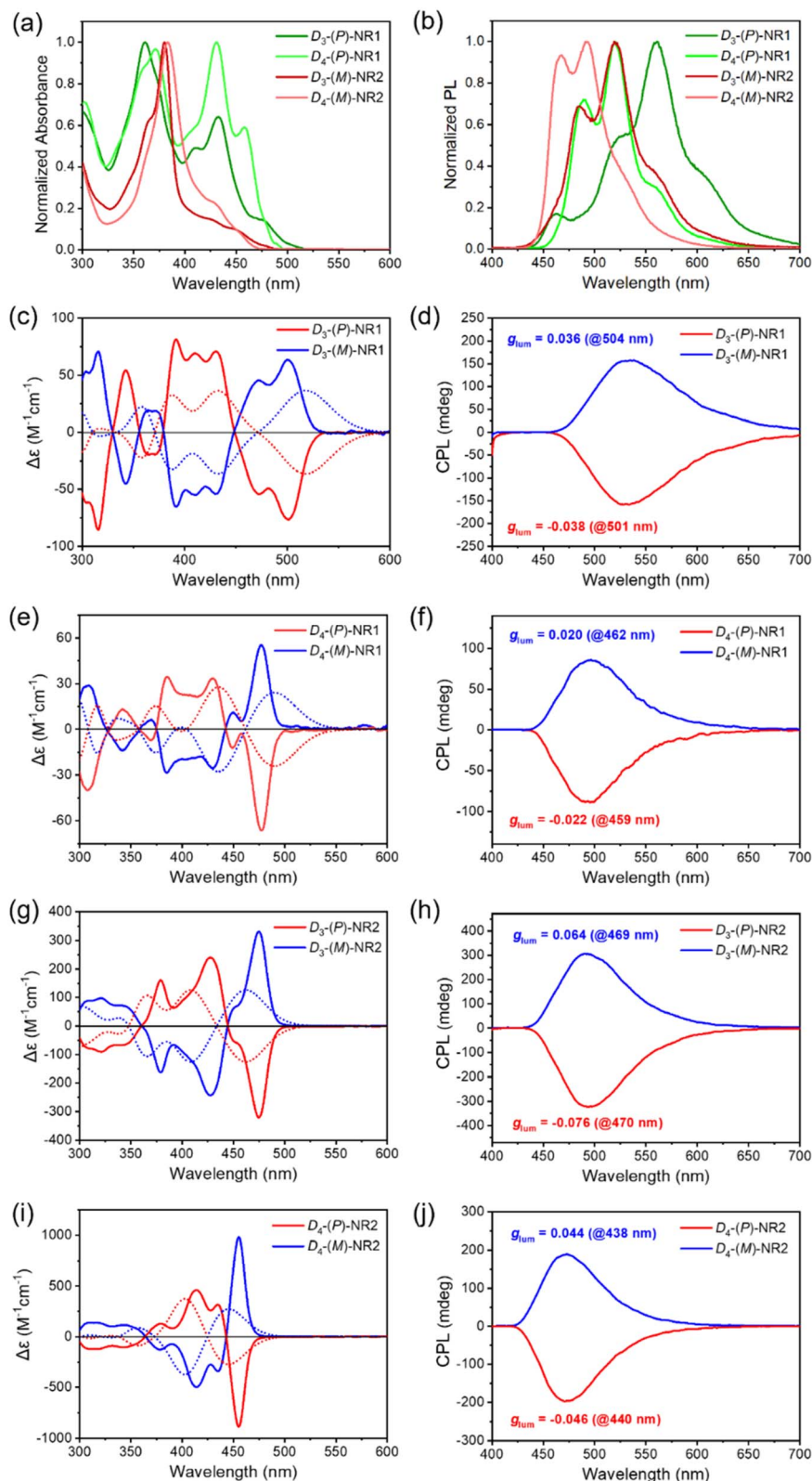


Fig. 5 The UV-Vis absorption spectra (a) and photoluminescence spectra (b) for  $D_3$ -(P)-NR1,  $D_4$ -(P)-NR1,  $D_3$ -(M)-NR2 and  $D_4$ -(M)-NR2. The CD (left) and CPL (right) spectra for  $D_3$ -(P)-NR1 and  $D_3$ -(M)-NR1 (c and d),  $D_4$ -(P)-NR1 and  $D_4$ -(M)-NR1 (e and f),  $D_3$ -(P)-NR2 and  $D_3$ -(M)-NR2 (g and h),  $D_4$ -(P)-NR2 and  $D_4$ -(M)-NR2 (i and j) in toluene. Note: the dotted lines in the CD spectra are DFT-predicted ones.



43%, respectively. Notably, compared to the larger  $D_4$  nanorings, the smaller  $D_3$  nanorings exhibit red-shifted emission peaks and reduced quantum yields, similar to the size-dependent luminescence properties observed in CPP and methylene-bridged cycloparaphenylene (MCP) nanorings.<sup>67–69</sup>

Since the nanorings prepared *via* the chiral tether-guided approach possess uniquely defined configurations, chiral resolution is unnecessary, allowing direct testing of their chiroptical properties. The circular dichroism (CD) and circularly polarized luminescence (CPL) spectra of all nanorings and their enantiomers are shown in Fig. 5c–j. All measurements were conducted in dilute solutions ( $\sim 1 \times 10^{-5}$  M) to ensure the signals originated from single molecules rather than aggregates. Each pair of enantiomers exhibited mirror-image CD and CPL spectra. For the CD spectra, all *P*-helical nanorings displayed a negative Cotton effect near the bandgap, while all *M*-helical nanorings showed a positive Cotton effect. The theoretically calculated CD spectra matched well with the experimental results. We further compared the CD spectra of the fused-lactam nanorings  $D_3$ -(*P*)-NR1 and  $D_4$ -(*P*)-NR1 before and after heating at 100 °C for 24 hours (Fig. S72a), revealing nearly overlapping spectra. Since the fused-carbazole nanorings  $D_3$ -(*M*)-NR2 and  $D_4$ -(*M*)-NR2 decompose upon heating, we assessed their chiral stability at room temperature. After one week of storage, no significant changes were observed in their CD spectra (Fig. S72b). These experiments confirm the earlier theoretical predictions that these molecules generally possess high atropisomerization barriers (Fig. S65), ensuring excellent chiral stability. All nanorings exhibited strong CPL signals. Consistent with the CD signals near the bandgap, all *P*-helical nanorings displayed a negative Cotton effect in CPL, while all *M*-helical nanorings showed a positive Cotton effect. Additionally, all nanorings demonstrated large luminescence dissymmetry factors ( $g_{\text{lum}}$ ), exceeding  $10^{-2}$  in magnitude. Notably,  $D_3$ -(*P*)-NR2 exhibited a remarkably high  $g_{\text{lum}}$  of  $-0.076$ , making it one of the rare purely organic molecules with a large intrinsic  $g_{\text{lum}}$ . To understand why these nanorings generally exhibit large dissymmetry factors, we analyzed their  $S_1 \rightarrow S_0$  transitions by DFT. Fig. 6 illustrates their transition characteristics, revealing that all molecules possess a substantial magnetic transition dipole moment ( $m$ ) along the helical axis. The  $|m|$  values for  $D_3$ -(*P*)-NR1,  $D_4$ -(*P*)-NR1,  $D_3$ -(*M*)-NR2 and  $D_4$ -(*M*)-NR2 are 8.32, 12.55, 9.14, and 14.18 Bohr magnetons ( $\mu_B$ ), respectively—among the largest reported for organic chiral molecules.<sup>70</sup> Moreover, the electric ( $\mu$ ) and magnetic ( $m$ ) transition dipole moments are consistently aligned either parallel or antiparallel. In *P*-helical nanorings, the angles between  $\mu$  and  $m$  are  $179.5^\circ$  and  $180^\circ$ , whereas in *M*-helical nanorings, they are  $1.3^\circ$  and  $0^\circ$ . These factors collectively contribute to the high  $g_{\text{lum}}$ . Furthermore, the carbazole-type nanorings exhibited larger  $m$  and smaller  $\mu$  compared to the lactam-type nanorings, explaining their higher  $g_{\text{lum}}$  values. In both carbazole- and lactam-type nanorings,  $m$  increased with ring size, consistent with the reported “molecular solenoid inner area rule”.<sup>70</sup> From  $D_3$  to  $D_4$  nanorings, the increase in  $m$  was comparable to that in  $\mu$ , resulting in minor changes (or even slight decreases) in  $g_{\text{lum}}$ . However, based on theoretical calculations by Long *et al.*, synthesizing higher-order

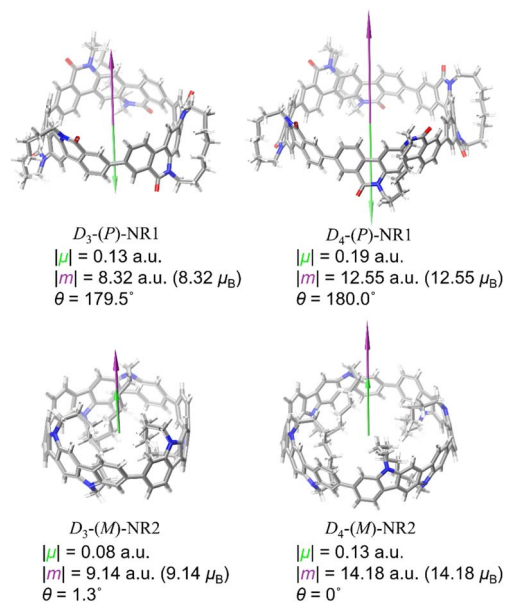


Fig. 6 The optimized geometry of  $S_1$  state and the  $S_1 \rightarrow S_0$  transition characteristics for  $D_3$ -(*P*)-NR1,  $D_4$ -(*P*)-NR1,  $D_3$ -(*M*)-NR2 and  $D_4$ -(*M*)-NR2. Note: “a.u.” denotes the atomic unit; the vector arrow for  $\mu$  is scaled up by a factor of 60.

$D_n$ -symmetric nanorings could further enhance  $m$  relative to  $\mu$ , potentially leading to breakthroughs in  $g$ -values.<sup>50</sup>

## Conclusion

In summary, we have developed a chiral tether-guided strategy to selectively prepare  $D_n$ -symmetric chiral conjugated nanorings. The high selectivity stems from the chiral tether induced strain, which amplifies the energy differences among the various atropisomers of the nanorings, thereby directing one  $D_n$ -symmetric isomer to become the thermodynamically favored product. All synthesized  $D_3$  and  $D_4$  nanorings exhibit exceptional circularly polarized luminescence properties, with a maximum luminescence dissymmetry factor reaching 0.076 and photoluminescence quantum yields up to 80%, demonstrating their great potential as high-performance CPL emitters. In the future, we will extend this strategy to synthesize higher-order  $D_n$ -symmetric nanorings, which may lead to breakthroughs in the development of organic molecules with intrinsically giant  $g_{\text{lum}}$ .

## Author contributions

Z. X. conceptualized the work. T. A., Q. Y., Y. S., Z. D., X. Z. synthesized the compounds. T. A. and Y. W. performed the theoretical calculations. J. Y., Z. X., Y. G., Z. H., C. Z. and L. D. directed the experiments and discussed the results. Z. X., Z. H., M. L., C. Z. and L. D. directed the project. Z. X. wrote the manuscript.

## Conflicts of interest

The authors declare no conflict of interest.



## Data availability

CCDC 2440960, 2440962 and 2440966 contain the supplementary crystallographic data for this paper.<sup>†1a-c</sup>

All other data supporting the findings of this study are available within the article and its supplementary information (SI), as well as available from the corresponding authors upon reasonable request. Supporting information available: materials synthesis and characterization; theoretical calculation; Scheme S1–5, Fig. S1–72, Table S1. See DOI: <https://doi.org/10.1039/d5sc06445g>.

## Acknowledgements

We thank the National Key Research and Development Program of China (2022YFB3803300, 2023YFE0116800), National Natural Science Foundation of China (22571057), and Beijing Natural Science Foundation (IS23037) for financial support. This work is supported by High Performance Computing Center of NCNST, China.

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