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chiroptoelectronic and chirospintronic

materials such as helicenes and their

derivatives,^[1] chiral nanoparticles,^[2] chiral nanoclusters,^[3] chiral carbon nanotube

fragments,^[4] etc. have been reported.

While it is still in the quite early infant

stage, these chiral materials play important

roles in advanced technologies such as

circularly polarized photodetector,[5] 3D display^[6] and chiro-spintronic devices^[7]

since they can demonstrate unique chirop-

tical properties,[8] like circular dichroism,[9]

circularly polarized photoluminescence,[10]

chiral-induced spin selectivity^[11] and

Among all these unique chiroptical properties, circular dichroism (CD) originates

topological quantum properties,^[12] etc.

Chiral Cylindrical Molecule with Absorption Dissymmetry Factor towards Theoretical Limit of 2

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Chiral molecules play important roles in advanced materials and technologies owing to their unique chiroptical properties. How to design and construct the best chiral molecules with intrinsically strong chiroptical properties is still a great challenge since there is an intrinsic contradiction between the large absorption dissymmetry factor and oscillator strength. In this work, through a systematic theoretical investigation, it is found that chiral cylindrical molecules could overcome this problem through accumulating the electric and magnetic transition dipole moment along the cylindrical axis direction while canceling them in other directions. Among all the investigated structures, (M)-[8]CC_{2.8} is found to exhibit the best chiroptical properties with $g_{\rm abs}$ of 0.71 and oscillator strength of 0.032. To the best of our knowledge, this is the best chiral molecule with both large dissymmetry factor and oscillator strength. Further increasing the repeating units, the gabs can even reach the theoretical limit of 2 for (M)-[28]CC_{2.81} together with a large oscillator strength of 0.134. The result offers the exciting opportunities for designing and synthesizing chiral materials with truly large intrinsically chiroptical properties toward real applications in chiroptoelectronic and chiro-spintronic devices.

1. Introduction

Chirality is a universal and fundamental feature of nature, which is closely related to life phenomena and exists in all aspects of nature and our lives. On the other hand, various

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and other chiroptoelectronic and chirospintronic devices. Toward the real application of chiral materials in CPPD, it is highly needed to develop chiral materials with intrinsically strong chiroptical properties: large rotatory strength and absorption dissymmetry factor as well as strong absorption strength

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from the difference in absorptivity of leftand right-handed circularly polarized light, which is the most basic property of chiral materials and widely used to evaluate the capability of chiral materials to construct the circularly polarized photodetectors (CPPD)



(oscillator strength). However, up to date, there is still no reliable strategy or design principle available for developing chiral materials with intrinsically strong chiroptical properties. Most of the reported chiral molecules, including single and multiple helicenes, exhibit a small absorption dissymmetry factor (typically in a range of 10^{-4} to 10^{-2}).^[13] Together with the synthetic challenge of these materials, therefore, it is highly important to employ theoretical calculations to establish the structure-property relationship of chiral molecules, and in advance screen the best possible chiral molecules with intrinsically strong chiroptical property prior to synthesis, which could significantly accelerate the discovery of chiral molecules with strong optical chirality and also save the power and time-cost during material synthesis.^[14] Time-dependent density functional theory (TDDFT) calculations provide a reliable description and prediction of circular dichroism in many realistic chemical systems, which could satisfy both moderate accuracy and computational efficiency.^[15] In this work, we are aiming to screen the best chiral molecules with intrinsically strong chiroptical properties and establish the structureperformance relationship between the molecular structure and chiroptical property of these molecules based on TDDFT calculations, and hopefully provide some intrinsically strong chiroptical molecules in theory.

Essentially, circular dichroism ($\Delta \epsilon$) is theoretically calculated based on Equation 1,^[16]

$$\Delta \epsilon (E) = \frac{1}{2.297 \times 10^{-39} \times \sqrt{2\pi\sigma}} \sum_{i}^{n} E_{i} R_{i} e^{-\left[\frac{(E-E_{i})}{2\sigma}\right]^{2}}$$
(1)

where E_i and R_i are the energy and rotatory strength of the *i*th transition and σ is the line width of the absorption band. For a single molecule with random orientations, R_i is calculated by the imaginary part of the scalar product between the relevant electric (μ_e) and magnetic transition dipole moments (μ_m) based on Equation 2,^[17]

$$R_{\rm i} = Im \left(\mu_{\rm e} \cdot \mu_{\rm m}\right) = \left|\mu_{\rm e}\right| \left|\mu_{\rm m}\right| \cos\theta \tag{2}$$

where θ is the angle between these two vectors. This equation is also known as the Rosenfeld equation,^[18] which indicates that a strong chiroptical response can be achieved by maximizing both the electric and magnetic transition dipole moments and simultaneously keeping their mutual angle far away from 90°.^[13] Meanwhile, the absorptivity (ϵ) is determined by Equation 3,

$$\varepsilon = \frac{2.174 \times 10^8}{\sigma} \sum_{i}^{n} f_i e^{-2.772 \left[\frac{(E-E_i)}{\sigma}\right]}$$
(3)

where f_i is the oscillator strength of the *i*th transition. The degree of chirality is further quantified by the absorption dissymmetry factor (g_{abs}). For a given transition *i*, the g_{abs} is deducted according to its definition from Equations 1 and 2,

$$|g_{abs}| = \frac{|\Delta \varepsilon|}{\varepsilon} \propto \frac{E_i \cdot |R_i|}{f_i}$$
(4)

As shown in Equation 4, the absolute value of dissymmetry factor $|g_{abs}|$ is proportional to the excitation energy required for the

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Figure 1. Color map of the relationship between oscillator strength (f_i) , excitation energy (E_i) , rotatory strength (R_i) and the absorption dissymmetry factor (g_{abs}) of chiral molecules.

*i*th transition (E_i) and the corresponding R_i , and inversely proportional to f_i . The relationship between $E_i \cdot R_i$ and f_i , and the respected $|g_{abs}|$ is mathematically solved and shown in **Figure 1**, the larger $|g_{abs}|$ falls into the region of smaller f_i and larger product of $E_i \cdot R_i$, while the smaller $|g_{abs}|$ falls into the region of larger f_i and smaller product of $E_i \cdot R_i$. Therefore, when the excitation energy of incident light is fixed, larger $|g_{abs}|$ can be obtained through increasing R_i while decreasing f_i . However, this is paradoxical since both R_i and f_i possess a positive correlation to the electric transition dipole (μ_e); decreasing μ_e could reduce both R_i and f_i . Most importantly, if the f_i of the respected optical transition is too small ($f_i < 0.01$, forbidden transition), this transition will beyond the detection limit of CD spectroscopy. Even $|g_{abs}|$ is theoretically becoming larger in this case, which is useless towards real application in chiroptoelectronic and chiro-spintronic devices. For example, the predicted g_{abs} of the proposed (R, R, R, R)-[8]cycloparaphenylene could reach 1.067, but the respected optical transition is forbidden (f_i is only 0.0009).^[19] Therefore, future work should focus on increasing both f_i and R_i at the same time towards larger $|g_{abs}|$.

Among all the reported chiral molecules, chiral cylindrical molecules are proven to exhibit the best chiroptical responses (as shown in Figure 2), which is very promising toward real application in chiroptoelectronic and chiro-spintronic devices.^[26] In 2011, Itami et al.^[21] reported the synthesis of chiral carbon nanoring by inserting the acene units (2,6-naphthylene, 2,6anthrylene and 2,8-tetracenylene) into [n]Cycloparaphenylenes ([n]CPP). However, unfortunately, the enantiomers were not separated. In the same year, Isobe et al.^[22] reported the synthesis of [4]cyclo-2,8-chrysenylene ([4]CC_{2.8}), which is the first demonstration of the bottom-up cyclophenacene congeners with complete isolation and identification of the enantiomers. An impressively large absorption dissymmetry factor of -0.167 and +0.166was observed for (P)- and (M)-(12,8)-[4]CC, respectively.^[27] This indicates that chiral cylindrical molecules are very promising towards the strong chiroptical property.^[28] Since then,

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Figure 2. The representative structures of carbon nanotube fragments. Before 2011, the research on chiral nanotube fragment mainly focuses on the achiral counterparts.^[20] In 2011, Itami et al. reported the synthesis of [13]CPPN based chiral carbon nanorings.^[21] Later in the same year, Isobe et al. demonstrated the first bottom-up cyclophenacene congeners ([4]cyclo-2,8-chrysenylene, [4]CC_{2,8}) with the complete isolation and identification of the enantiomers, and investigated their chiroptical properties.^[22] Since then, various chiral cylindrical molecules were reported by Isobe et al.,^[23] Miao et al.,^[24] and Du et al.^[25]

various chiral cylindrical molecules have been synthesized and investigated by different groups worldwide (as shown in Figure 2), but their absorption dissymmetry factor does not exceed that of (P)- and (M)-(12,8)-[4]CC. Therefore, it is highly needed to systematically investigate the structure-chiroptical property relationship of chiral cylindrical molecules and screen out the best chiral molecules with larger absorption dissymmetry factor. However, no such work is performed up to date. In this work, we have systematically investigated the chiroptical properties of a wide range of chiral cylindrical molecules with various segments ([n]cyclo-2,8-chrysenylene ([n]CC_{2.8}), [n]cyclo-3,9chrysenylene ([n]CC_{3,9}), [n]cyclo-2,8-naphthacenylene ([n]CN_{2,8}), and [n]cyclo-3,9-tetrapheneylene ([n]CT_{3,9}), their structures are shown in Figure 3a) via theoretical calculation. It is found that diverse structures with different arrangements, distinct connection positions, and repeating numbers all have a significant influence on the chiroptical properties of the respective cylindrical molecules. Among all the investigated structures, (M)-[8]CC2.8 is predicted to exhibit the best chiroptical properties with rotatory strength exceeding 5.26×10^{-37} erg esu cm G⁻¹, g_{abs} up to 0.71 and oscillator strength of 0.032. To the best of our knowledge, this is the best chiral molecule with both large dissymmetry factor and oscillator strength. More importantly, further increasing the repeating units of (M)-[8]CC_{2,8}, the g_{abs} can even reach the theoretical limit of 2 for (M)-[28]CC_{2.8}. Finally, a balance between the absorption dissymmetry factor and oscillator strength is thoughtfully discussed. These results provide some

targeted molecules with great potential toward chiroptoelectronic and chiro-spintronic applications.

2. Results and Discussion

2.1. The Chemical Structures and Chiroptical Properties

The chiral molecules with unique 3D cylindrical structures (the molecular segments and their enantiomers) investigated in this work are shown in Figure 3. The building block of (M)- $[n]CC_{2.8}$, (-)-[*n*]CC_{3,9}, (*M*)-[*n*]CN_{2,8}, and (*P*)-[*n*]CT_{3,9} is 2,8-chrysene-diyl, 3,9chrysene-diyl, 2,8-naphthacenylene and 3,9-tetraphene-diyl, respectively (as shown in Figure S1, Supporting Information). Arranging different numbers of these building blocks in an annulus, a series of chiral cylindrical molecules with repeat units (*n*) from 4 to 8 are constructed (Figure 3b). The geometry structures of these chiral cylindrical molecules are optimized by density functional theory (DFT)^[29] at the RB3LYP/6-31 g (d, p) level,^[30] and the harmonic vibrational frequency analysis is performed to ensure that the fully optimized stationary point is found. Then the unique chiroptical properties of these chiral cylindrical molecules are calculated by TDDFT based on the optimized geometry with the same functional and basis set. Considering the chiroptical properties of the enantiomers are just opposite (as shown in Figure S2, Supporting Information), we only calculate the chiroptical properties of one enantiomer, (M)-[n]CC_{2.8}, (-)-[*n*]CC_{3,9}, (*M*)-[*n*]CN_{2,8} and (*P*)-[*n*]CT_{3,9} in this work. The

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Figure 3. Chiral cylindrical molecules. a) Chemical structures of (*M*)- $[n]CC_{2,8}$, $(-)-[n]CC_{3,9}$, $(M)-[n]CN_{2,8}$, $(P)-[n]CT_{3,9}$ investigated in this work. b) An example of (*M*)- $[4]CC_{2,8}$ based on unit vectors a_1 and a_2 and chiral vector $C_h = na_1+ma_2$ of carbon nanotube. c) The calculated rotatory strength and $|g_{abs}|$ for the $S_0 \rightarrow S_1$ transition of (*M*)- $[n]CC_{2,8}$ (n = 4-8).

optimized geometries and the predicted absorption and CD spectra of these chiral molecules are shown in Figures S3–S7 (Supporting Information).

Here, we take (*M*)- $[n]CC_{2,8}$ family (n = 4-8) as an example to illustrate the unique chiroptical properties of these chiral cylindrical molecules, and then compare their chiroptical properties with other chiral cylindrical molecules. As shown in Figure S7 (Supporting Information), the (M)-[n]CC_{2.8} families exhibit a strong Cotton effect (CE) in the calculated CD spectra. For example, (M)-[4]CC_{2.8} exhibits a characteristic positive-negative-positive transition from 320 to 480 nm, which is almost consistent with the experimental CD spectrum.^[22,27] The calculated rotatory strength of the $S_0 \rightarrow S_1$ transitions of (M)- $[n]CC_{2,8}$ is also shown in Figure 3c, which increases steadily with the repeating units from 4 to 8 and reaches 5.26×10^{-37} erg esu cm G⁻¹ for (*M*)-[8]CC_{2,8}. The calculated rotatory strength of (*M*)-[4]CC_{2.8} is 1.04×10^{-37} erg esu cm G⁻¹, which is well consistent with the experimental value of 1.01 $\times 10^{-37}$ erg esu cm G^{-1,[31]} confirming the reliability of our calculation results. As shown in Figure 3c, the $|g_{abs}|$ of the $S_0 \rightarrow S_1$ transitions of these molecules also exhibit a similar growing trend with the rotatory strength, and (M)-[8]CC_{2,8} exhibits an exceptionally large absorption dissymmetry factor of 0.71 at 419 nm. To the best of our knowledge, this is the largest predicted value that has been reported for chiral organic molecules with oscillator strength over $0.01^{[9a]}$.

2.2. Mechanism of the Large Absorption Dissymmetry Factor

The large g_{abs} of [8]CC_{2.8} encourages us to explore the detailed cooperation mechanism between electric and magnetic transition dipole moment. Thus, we decompose the total electric (magnetic) transition dipole moment of [8]CC2,8 into the contribution of each repeat unit (as shown in Figures S8 and S9, Supporting Information). Interestingly, most of the contributions of μ_e are along the Y-axis of the decomposed fragments (n = 3-7), however, when forming an intact ring as [8]CC_{2.8}, those contributions in the Y-axis direction cancel each other and only preserve a small component in the Z-axis direction (Figure 4a). On the contrary, the large contributions of μ_{m} are all along the Z-axis in all the fragments (from 3 to 7) and intact ^[8]CC_{2,8}, this accumulation effect leads to an enhancement of $\mu_{\rm m}$ (Figure 4b). The trends of $\mu_{\rm e}$ and $\mu_{\rm m}$ as repeat units increase are summarized in Figure 4c. According to the simplified Equation 7, it is obvious that the large $g_{\rm abs}$ of ^[8]CC_{2.8} is attributed to the reduced $\mu_{\rm e}$ but increased $\mu_{\rm m}$ (Figure 4d) with increasing the repeat units from 1 to 8. This further confirms the superiority of cylindrical structure to get strong chiroptical properties. As shown in Figure S10a,b (Supporting Information), both $|\boldsymbol{\mu}_{e}|$ and $|\boldsymbol{\mu}_{m}|$ grow significantly with increasing the repeat units of (M)-[n]CC_{2,8} (n = 4-8), and the increment of $|\boldsymbol{\mu}_{\mathrm{m}}|$ is more evident. Most importantly, the directions of both the $\mu_{\rm e}$ and $\mu_{\rm m}$ in (*M*)-[*n*]CC_{2.8} (*n* = 4–8) parallel to the cylindrical axis (Figure S11, Supporting Information), permitting the maximum $|\cos \theta|$ contribution.

As expected, the rotatory strength and $g_{\rm abs}$ are sensitive to the molecular fragments and connection positions. As shown in Figure 5a-c, a similar growing trend is also observed for the rotatory strength, absorption dissymmetry factor, oscillator strength, electric and magnetic transition dipole moment of the $S_0 \rightarrow S_1$ transition for (-)- $[n]CC_{3,9}$, (P)- $[n]CT_{3,9}$ and (M)- $[n]CN_{2,8}$ with increasing the repeating units. For the same hoop size (n), (M)-[n]CN_{2.8} systems exhibit larger electric transition dipole moment and oscillator strength than that of (-)- $[n]CC_{3,9}$ and (P)- $[n]CT_{3,9}$, while the (M)-[n]CC_{2.8} system exhibits the smallest electric transition dipole moment and oscillator strength. However, the trend for the magnetic transition dipole moments is reversed, (M)-[8]CC_{2.8} exhibits the largest magnetic transition dipole moment of 31.07×10^{-20} erg G⁻¹, while which is only 16.02×10^{-20} erg G⁻¹ for (*M*)-[8]CN_{2.8}. The electric and magnetic transition dipole moment for the $S_0 \rightarrow S_1$ transition of (*P*)-[*n*]CT_{3,9} and (-)- $[n]CC_{3,9}$ is paralleled ($\theta = 0^{\circ}$), while which is anti-paralleled for (*M*)-[*n*]CC_{2.8} and (*M*)-[*n*]CN_{2.8} (θ = 180°), respectively (as shown in Figures S11-S14, Supporting Information). Therefore, the rotatory strength and absorption dissymmetry factor of the $S_0 \rightarrow S_1$ transition of these molecules are only determined by the magnitude of electric and magnetic transition dipole moments (Equations 6 and 7). For the (M)-[n]CN_{2.8} families, the larger electric transition dipole moment and smaller magnetic transition dipole moment contribute to a larger rotatory strength comparable with (-)-[n]CC_{3,9} and (P)-[n]CT_{3,9} (as shown in Figures S15 and S16, Supporting Information). Meanwhile, the smaller electric transition dipole moment and the larger magnetic transition dipole





Figure 4. The contribution of the electric (magnetic) transition dipole moment of each repeat unit to the whole molecules. a) Electric transition dipole moment vector contributions (a.u.) from repeat unit n = 4 and 8 (magenta) and total (red) for (M)-[8]CC_{2,8}. b) Magnetic transition dipole moment vector contributions (a.u.) from repeat unit n = 4 and 8 (magenta) and total (red) for (M)-[8]CC_{2,8}. b) Magnetic transition dipole moment vector contributions (a.u.) from repeat unit n = 4 and 8 (cyan) and total (blue) for (M)-[8]CC_{2,8}. c) The relationship between the number of repeat units (n) and μ_m (in erg G⁻¹) of (M)-[8]CC_{2,8} (n = 1-8). d) The relationship between the number of repeat units (n) and $|g_{abs}|$ of (M)-[8]CC_{2,8} (n = 1-8).

moment of the $S_0 \rightarrow S_1$ transition of (M)- $[n]CC_{2,8}$ could also contribute a comparable rotatory strength, which further confirms that both larger electric and magnetic transition dipole moments are highly needed to increase the rotatory strength.

Furthermore, in order to investigate the limit of increasing the repeating units of (M)- $[n]CC_{2,8}$ on the absorption dissymmetry factor, the geometric structures of (M)- $[9]CC_{2,8}$, (M)- $[10]CC_{2,8}$, (M)- $[15]CC_{2,8}$ and (M)- $[20]CC_{2,8}$ were also optimized, it is found that magnetic transition dipole moment and absorption dissymmetry factor of the S₀ \rightarrow S₁ transition of these molecules can be further increased. For (M)- $[20]CC_{2,8}$, the magnetic transition dipole moment and absorption dissymmetry factor are increased to 124.97 × 10⁻²⁰ erg G⁻¹ and 1.47, respectively. Then, the correlation between the absorption dissymmetry factor, oscillator strength, and repeating units (**Figures 6**a and S17, Supporting Information) is fitted based on Equation 5. Based on the fitted results, (*M*)-[28]CC_{2.8} could achieve the theoretical limit of absorption dissymmetry factor ($g_{abs} = 2$) with oscillator strength of 0.134. Even it is very difficult to synthesize these molecules and they have complicated conformations and configurations, our work confirms that it is still possible to construct the strongest chiral molecules with an absorption dissymmetry factor approaching 2.

2.3. Correlation between Absorption Dissymmetry Factor, Rotatory Strength, and Oscillator Strength

The relationship between the $|g_{abs}|$ and $E_i \cdot R_i / f_i$ of $(M) \cdot [n] CC_{2,8}$, (-)- $[n] CC_{3,9}$, $(M) \cdot [n] CN_{2,8}$, $(P) \cdot [n] CT_{3,9}$ is shown in Figure 6a, and all points are fallen perfectly into a straight line, which further confirms the reliability of the proportional relationship shown in Equation 4. The relationship between $E_i \cdot R_i$ and f_i , and the respected $|g_{abs}|$ of $(M) \cdot [8] CC_{2,8}$, (-)- $[8] CC_{3,9}$, $(M) \cdot [8] CN_{2,8}$ and $(P) \cdot [8] CT_{3,9}$ is also shown in Figure 6b, the larger $|g_{abs}|$ of $(M) \cdot [8] CC_{2,8}$



(5)

Figure 5. The calculated results of the rotatory strength, absorption dissymmetry factor, oscillator strength, electric and magnetic transition dipole moment of the $S_0 \rightarrow S_1$ transition. a) (-)-[n]CC_{3,9}. b) (P)-[n]CT_{3,9}. c) (M)-[n]CN_{2,8}, n = 4-8. The contribution of the electric (magnetic) transition dipole moment of each repeat unit.

 $g_{abs} = 0.066n + 0.173$



SIMULATIONS



Figure 6. The structure–property relationship of the chiral cylindrical molecules investigated in this work. a) The correlation between absorption dissymmetry factor (g_{abs}) and repeating units (n) of (M)-[n]CC_{2,8}. b) The relationship between the $|g_{abs}|$, f_i and the ratio of $E_i \cdot R_i / f_i$ of the studied chiral cylindrical molecules. (c) Color map of the relationship between oscillator strength, $E_i \cdot R_i$ and $E_i \cdot R_i / f_i$ of (M)-[n]CC_{2,8}, (-)-[n]CC_{2,9}, (M)-[n]CC_{2,9}, and (P)-[n]CT_{3,9}.

falls into the region of modest f_i and larger product of $E_i \cdot R_i$, while the smaller $|g_{abs}|$ of (M)-[8]CN_{2.8} falls into the region of larger f_i and smaller product of $E_i \cdot R_i$. Therefore, constructing the chiral cylindrical molecules with a larger diameter (increase the repeat unit) is an effective strategy to increase the magnetic transition dipole moment, and meanwhile maintain a modest oscillator strength. Future work should focus on increasing both f_i and R_i of chiral molecules at the same time, thus the larger $|g_{abs}|$ towards real application.

3. Conclusion

In summary, the chiroptical properties of a series of unique chiral cylindrical molecules with different repeating units were systematically investigated in this work. It is found that the chiral cylindrical molecules could overcome the intrinsic contradiction between large absorption dissymmetry factor and oscillator strength through accumulating the electric and magnetic transition dipole moment along the cylindrical axis direction while canceling them in other directions. Therefore, strong chiroptical properties can be obtained through rationally designing and screening the best chiral cylindrical molecules. Among all the investigated structures, (M)-[8]CC_{2,8} is predicted to exhibit an extremely large (two order than the state of the art) record absorption dissymmetry factor of 0.71 together with a modest oscillator strength of 0.032. To the best of our knowledge, this is the best chiral molecule with both large absorption dissymmetry factor and oscillator strength. Further increasing the repeating units of (*M*)-[8]CC_{2,8}, the g_{abs} can even reach the theoretical limit of 2 for (*M*)-[28]CC_{2,8}, while its synthesis is more challenging than that of (*M*)-[8]CC_{2,8}. Future work should focus on designing and synthesizing these cylindrical molecules with both large dissymmetry factor and oscillator strength towards real applications in chiroptoelectronic and chiro-spintronic devices.

4. Experimental Section

The geometry structures of (M)- $[n]CC_{2,8}$, (-)- $[n]CC_{3,9}$, (M)- $[n]CN_{2,8}$, and (P)- $[n]CT_{3,9}$ (n = 4-8) are optimized by density functional theory $(DFT)^{[29]}$ at the RB3LYP/6-31 g (d, p) level,^[30] and the harmonic vibrational frequency analysis is performed to ensure that the fully optimized stationary point is found. Then the unique chiroptical properties of these chiral cylindrical molecules are calculated by TDDFT based on the optimized geometry with the same functional and basis set. As for the prediction of (M)- $[9]CC_{2,8}$, (M)- $[10]CC_{2,8}$ and (M)- $[20]CC_{2,8}$, in consideration of computing costs and efficiency, those geometries optimizations are all finished within the convergence criteria at the RB3LYP/6-31g(d) level. Further, the TDDFT calculation is performed at the same level. The lowest 60 states are considered for (M)- $[9]CC_{2,8}$ and (M)- $[10]CC_{2,8}$, while the lowest 5 states for and (M)- $[20]CC_{2,8}$.

The absorption dissymmetry factor (g_{abs}) of the chiral cylindrical molecules in this work is calculated based on Equation 6,

$$g_{abs} = \frac{4 |\mu_e| |\mu_m| \cos\theta}{|\mu_e|^2 + |\mu_m|^2}$$
(6)

Evidently, g_{abs} is a dimensionless quantity and within the range from -2 to +2. When the vectors of μ_e and μ_m are equal to each other in length and oriented in either the parallel or antiparallel direction (to maximize the $|\cos \theta|$), the absolute value of g_{abs} can be reached to the maximum value of 2. While in theory, the magnitude of μ_m is typically far smaller than that of μ_e in most chiral molecules, so Equation 7 can be simplified as:

$$g_{abs} \approx 4 \frac{|\mu_m| \cos\theta}{|\mu_e|} \tag{7}$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

absorption dissymmetry factor, chiral cylindrical molecule, circular dichroism, oscillator strength, rotatory strength

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