Chiral Pentaphenylpyrrole Derivatives with Aggregation-Induced Emission Enhancement and Aggregation-Induced Circular Dichroism and Their Helical Self-assembly

Yuanyuan Wang ^{1,a}, Longlong Zhang ^{2,b}, Junge Zhi ^{1,*}

¹School of Chemistry and Chemical Engineering, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Beijing Institute of Technology, Beijing, China.

²School of Chemistry and Chemical Engineering, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Beijing Institute of Technology, Beijing, China.

Abstract: A pair of enantiomers (*S*)-P5PdiAM and (*R*)-P5PdiAM containing two chiral substituents, and their raceme rac-P5PdiAM were synthesized by introducing (*R*)-/(*S*)- or racemic 1-phenylethylamine into 1-biphenyl-2,3,4,5-tetraphenylpyrrole. The target compounds all show weak aggregation-induced emission enhancement (AIEE) characteristics in the DMSO/H₂O mixed system, indicating that the introduction of chirality hardly affect the photophysical properties of the compound. In addition, the chiral compounds (*S*)-P5PdiAM and (*R*)-P5PdiAM show strong circular dichroism (CD) signals in THF/H₂O mixed solution with a water fraction of 70%, that is, they exhibit aggregation-induced circular dichroism characteristics (AICD). Because the aggregates of (*S*)-P5PdiAM and (*R*)-P5PdiAM emit weakly, there is no circularly polarized luminescence (CPL) signals upon aggregation. The chiral compounds (*S*)-P5PdiAM and (*R*)-P5PdiAM can self-assemble to form helical nanofibers in a THF/H₂O mixture with a water fraction of 70%, while the racemic rac-P5PdiAM assembled to form nano-particles, indicating that chiral substituents have a great influence on the self-assembly and the morphologies of the nano-aggregates.

1 Introduction

In 2001, Tang's research group discovered a compound—hexaphenyl silole derivative (HPS), which hardly emits light in dilute solutions, but greatly enhances luminescence in concentrated solution and solid state, defined as "aggregation-induced emission" (AIE) phenomenon [1]. The luminescence mechanism of Silole is different from other structures of luminescence materials, due to the AIE effect. A series of organic light-emitting materials with novel structure, high luminous efficiency and AIE/AIEE characteristics have been redesigned and synthesized by further exploring the theory and mechanism on the basis of Silole's research. The aggregation process restricted the vibration and rotation of the intramolecular groups, resulting in a decrease in non-radiative energy transfer, which can effectively increase the fluorescence quantum yield of the luminescent materials in the aggregation states. The discovery of AIE has solved the major problem of aggregation caused quenching (ACQ) in luminescent materials to a certain extent, and has greatly increased the application range of fluorescent materials [2-5]. More and more researchers are committed to designing and synthesizing new AIE compounds, and adjust the luminescence behavior by

adjusting the molecular aggregation state, because the compounds with AIE characteristics have broad application prospects. The target products have both AIE properties and special optical properties by introducing chiral groups into AIE unit, thereby obtaining AIE fluorescent materials with special morphologies. New chiral materials exhibit excellent CD and CPL signals, and have potential applications in optical devices, chiral recognition, monitoring and separation [6-7].

In the previous work, several chiral pentaphenylpyrrole and triphenylpyrrole derivatives were obtained by introducing *R*-/*S*-racemic 1-phenylethylamine into the multiarylpyrrole. The results show that the chiral compounds not only retain the original AIEE properties, but also have optical activities such as CD and CPL and self-assemble to form spiral nanofibers [8-9]. Therefore, we designed and synthesized chiral pentaphenylpyrrole derivatives with two chiral groups by introducing *R*-/*S*-racemic 1-phenylethylamine into the 3,4-position of pentaphenylpyrrole, and further investigate the effects of the chiral groups on the photophysical properties, optical activity, and self-assembly behavior of the target multiarylpyrrole derivatives.

^aemail: wyybit@126.com, ^bemail: 986134393@qq.com

*Corresponding author's e-mail: zhijunge@bit.edu.cn

2 Materials and Methods

The target compounds (*S*)-P5PdiAM, (*R*)-P5PdiAM, and rac-P5PdiAM (Scheme 1) were synthesized by introducing (*R*)-/(*S*)- or racemic 1-phenylethylamine into 1-biphenyl-2,3,4,5-tetraphenylpyrrole.

All of chemicals were purchased from J&K Company. Solvents and reagents were purchased from Beijing Chemical Reagent Company and were used as received without further purification.

¹H NMR spectra were measured on a Bruker AV 400 spectrometer. The UV-vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer. The fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. CD spectra were taken on a JASCO J-810 spectrometer. Circularly polarized luminescence (CPL) spectra were taken on a JASCO CPL-200 spectrofluoropolarimeter. The morphologies of the nano-aggregates were observed by a field-emission scanning electron microscope (FE-SEM, JEOL S-6700).

Scheme 1 The structures of the chiral target compounds.

Figure 1 (a) Fluorescence spectra of (*S*)-P5PdiAM in DMSO/H₂O mixtures with different f_w , (b) Plots of relative emission intensities (I/I_0) versus f_w for (*S*)-P5PdiAM (10 μ M)

Figure 2 is a comparison diagram of the relative fluorescence intensity (I/I_0) of (*S*)-P5PdiAM, (*R*)-P5PdiAM and rac-P5PdiAM with different f_w . The three compounds exhibit similar photophysical properties in the DMSO/H₂O mixtures, all have weak AIEE properties, indicating that the introduction of chiral groups have little impact on the AIEE properties. But when f_w is higher than 50%, the I/I_0 values of the chiral compounds are larger than that of the racemic compound. This is mainly due to the fact that the chiral compounds can self-assemble to

3 Results & Discussion

3.1 Aggregation-induced emission enhancement (AIEE)

Figure 1 depicts the fluorescence spectra of (*S*)-P5PdiAM in DMSO/H₂O mixed solutions. When the water fraction (f_w) is less than 40%, the increase of polarity of the mixed solution can intensify the loss of non-radiative energy, thus the fluorescence intensity decreases. When the f_w reaches 50%, the formation of aggregates with compacted molecular packing restrict the intramolecular movement and the non-radiative energy transferences, resulting in an enhancement of the fluorescence intensity. However, the enhanced emission intensity is still lower than the fluorescence intensity in pure DMSO solution, and the fluorescence intensity drops significantly after the f_w is higher than 70%. Therefore, (*S*)-P5PdiAM also displays weak AIEE properties in the DMSO/H₂O mixtures [2-4]. In addition, the fluorescence spectral variations for the other compounds are consistent with that of (*S*)-P5PdiAM, indicating the similar AIEE properties of (*R*)-P5PdiAM and rac-P5PdiAM.

form aggregates with regular molecular packing, thereby restricting the movement of intramolecular groups more effectively, and the spatial structure of chiral groups also restricts the intramolecular movement synergistically, resulting in a more significant emission enhancement of chiral compounds [2-4].

Figure 2 Plots of I/I_0 versus f_w for target compounds.

3.2 Aggregation-induced circular dichroism (AICD)

(S)-P5PdIAM show strong CD signals in the THF/H₂O

Figure 3 CD spectra of (S)-P5PdIAM and (R)-P5PdIAM in the THF/H₂O mixtures with different f_w (10 μ M)

3.3 Self-assembly of chiral compounds

The morphologies of the aggregates were studied to explore their helical self-assembly for the two enantiomers (S)-P5PdIAM, (R)-P5PdIAM. As shown in figure 4, (S)-P5PdIAM self-assembles to form helical nanofibers with the left-handed screw sense, which with an average width of about 100 nm. (R)-P5PdIAM also forms spiral

nanofibers with an average width of 50-100 nm, which exhibit right-handed screw sense. However, no helical nanofibers but only nanoparticles were observed for the racemic rac-P5PdIAM. The result illustrates that the induction effect of chiral groups not only makes the chiral compounds produce strong CD signals, but also form nanofibers with helical conformation upon aggregation in the THF/H₂O mixed solution^[9-11].

Figure 4 SEM images of the nano-aggregates for (S)-P5PdIAM(a), (R)-P5PdIAM(b), rac-P5PdIAM(c) (f_w = 70%)

4 Conclusions

In summary, two chiral (S)-P5PdIAM, (R)-P5PdIAM, and

their raceme rac-P5PdIAM were synthesized by introducing (R)-/(S)- or racemic 1-phenylethylamine into pentaphenylpyrrole. The three compounds (S)-P5PdIAM, (R)-P5PdIAM and rac-P5PdIAM exhibit weak AIEE

feature in DMSO/H₂O mixed solutions. More importantly, the chiral compounds (*S*)-P5PdiAM and (*R*)-P5PdiAM have strong CD signals in the THF/H₂O mixture at f_w of 70%, that is, they exhibit aggregation-induced circular dichroism (AICD) and can self-assemble to form helical nanofibers in the THF/H₂O mixtures, which illustrates they have potential applications in chiral recognition and separation.

Acknowledgments

The authors are grateful for the support received from the National Foundation of China (No. 21374010).

References

1. Luo, J.D., Xie, Z.L., Cheng, L., Qiu, C.F., Zhan, X.W., Liu, Y.Q., Zhu, D.B., Tang, B.Z. (2010) Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.*, 1740-1741.
2. Mei, J., Leung, N.L.C., Kwok, R.T.K., Lam, J.W.Y., Tang, B.Z. (2015) Aggregation-Induced Emission: Together we shine, united we soar. *Chem. Rev.*, 115:11718-11940.
3. Zhao, Z., Zhang, H.K., Lam, J.W.Y., Tang, B. Z. (2020) Aggregation-induced emission: new vistas at the aggregate level. *Angew. Chem. Int. Ed.*, 59: 9888-9907.
4. Cai, X.L., Liu, B. (2020) Aggregation-induced emission: recent advances in materials and biomedical applications. *Angew. Chem. Int. Ed.*, 59: 9868–9886.
5. Wang, Y., Nie, J., Fang, W., Yang, L., Hu, Q., Wang, Z., Sun, J.Z., Tang, B.Z. (2020) Sugar-based aggregation-induced emission luminogens: design, structures, and applications. *Chem. Rev.*, 120: 4534-4577.
6. Roose, J., Tang, B.Z., Wong, K.S. (2016) Circularly-polarized luminescence (CPL) from chiral AIE molecules and macrostructures. *Small*, 12: 6495–6512.
7. Feng, H.T., Liu, C.C., Li, Q.Y., Zhang, H.K., J. Lam, W.Y., Tang, B.Z. (2019) Structure, Assembly, and Function of (Latent)-Chiral AIEgens. *ACS Mater. Lett.*, 1: 192-202.
8. Liang, K.C., Dong, L.C., Jin, N., Chen, D.D., Feng, X., Shi, J.B., Zhi, J.G., Tong, B. Dong, Y.P. (2016) The synthesis of chiral triphenylpyrrole derivatives and their aggregation-induced emission enhancement, aggregation-induced circular dichroism and helical self-assembly. *RSC Adv.*, 6: 23420-23427.
9. Zhang, L.L., Liang, K.C., Dong, L.C., Yang, P.P., Li, Y.Y., Feng, X., Zhi, J.G., Shi, J.B., Tong, B., Dong, Y.P. (2017) Aggregation-induced emission enhancement and aggregation-induced circular dichroism of chiral pentaphenylpyrrole derivatives and their helical self-assembly. *New J. Chem.*, 41: 8877-8884.
10. Li, H.K., Cheng, J., Zhao, Y.H., Lam, J.W., Wong, Y.K.S., Wu, H.K., Li, B.S., Tang, B. Z. (2016) L-Valine methyl ester-containing tetraphenylethene: aggregation-induced emission, aggregation-induced circular dichroism, circularly polarized luminescence, and helical self-assembly. *Mater. Horiz.*, 1: 518-521.
11. Li, H.K., Cheng, J., Deng, H.Q., Zhao, E.G., Shen, B., Lam, J.W.Y., Wong, K.S., Wu, H. K., Li, B.S., Tang, B.Z. (2019) Aggregation-induced chirality, circularly polarized luminescence, and helical self-assembly of a leucine-containing AIE luminogen. *J. Mater. Chem. C*, 3: 2399-2404.