

Chiroptical Materials with Aggregation-Induced Emission (AIE) Characteristic: Fundamental Research and Application

Haoke Zhang, Jingzhi Sun, Anjun Qin*, Benzhong Tang*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering,
Zhejiang University, Hangzhou 310027, China

*Anjun Qin, Benzhong Tang, E-mail: qinaj@zju.edu.cn; tangbenz@ust.hk



Introduction

As a branch of organic luminophor, chiroptical materials play an indispensable role in the areas of bio-sensor, bio-detection and highly sophisticated optical devices. However a fatal defect lives in the general organic luminescent compounds – aggregation-caused quenching (ACQ), as in the most cases this kind of materials will be used in the solid state. We have researched on it for more than ten years, thankfully several types of aggregation-induced emission (AIE) materials have been developed, such as 1,1-Dimethyl-2,3,4,5-tetraphenylsilole (Silole) and tetraphenylethene (TPE), they have high quantum yield in the aggregation state. We and other groups have proved its mechanism was restriction of intramolecular motion (RIM), as its propeller-shaped π -conjugated configuration can prevent the formation of excimer and π - π stacking in the aggregation state.

Combining Binaphthol (BINOL) with tetraphenylethene (TPE) to generate excellent chiroptical materials. The synthetic compounds have high quantum yield in solid state, which have typical aggregation-induced emission (AIE) characteristic. But contrary to traditional chiroptical AIE molecules, they present abnormal aggregation-annihilation circular dichroism (AACD), and we have proved it was caused by the change of twist angle between two naphthalene rings (Figure 1). Then through locking two naphthalene rings, we have got the polymers with excellent chiroptical properties in the solid-state.

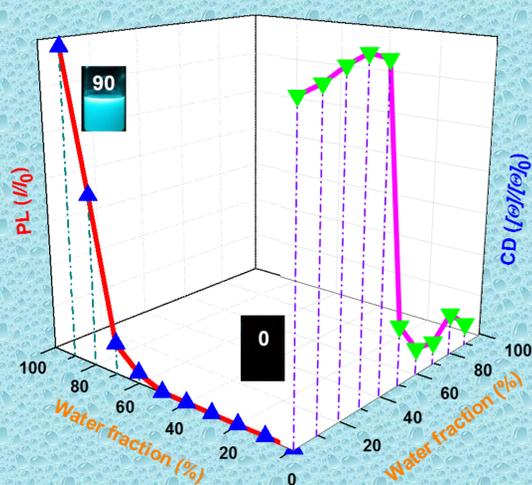


Figure 1. Illustration for the processes of AIE and AACD.

Results and Discussion

Part I --- Fundamental Research

Firstly we have designed and synthesized the compound 6,6'-DTPE-BINA(R). We hoped chirality could transfer to TPE from BINOL, at the same time, two TPE groups would endow the molecule with AIE performance. Seen from figure 2, 6,6'-DTPE-BINA(R) was a typical AIE molecule with a high AIE factor (700).

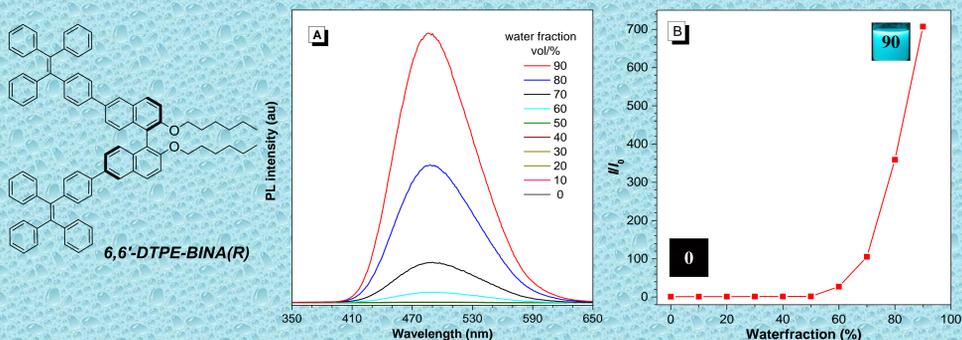


Figure 2. A) PL spectra of 6,6'-DTPE-BINA(R); B) Plots of I/I_0 versus the different water fraction (THF, $c = 10^{-5}$ M). I : maximum PL intensity in each plot, I_0 : maximum PL intensity at $f_w = 0\%$, $\lambda_{ex} = 330$ nm, insets: photographs of solution with different water fraction irradiated with 365 nm UV lamp.

Then we found 6,6'-DTPE-BINA(R) had the property of AACD. Through further research, we realized this phenomenon had no relationship with TPE, which was just the special property of BINOL's derivatives. Meanwhile, we have found it was caused by the change of twist angle between two naphthalene rings in the process of aggregation. When we locked the angle through phosphate group, this phenomenon disappeared.

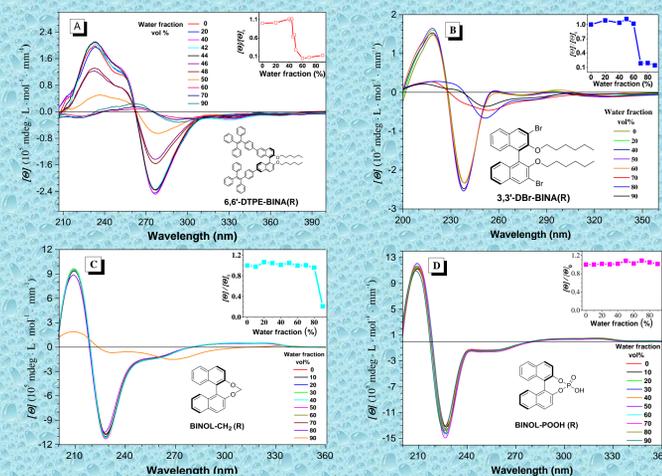


Figure 3. CD spectra of compounds A) 6,6'-DTPE-BINA(R), B) 3,3'-DBr-BINA(R), C) BINOL-CH₂(R), and D) BINOL-POOH(R) in different water fraction (THF/H₂O, $c = 10^{-4}$ M); Insets: Plots of $[\theta]/[\theta]_0$ versus water fraction for the three compounds, these values of $[\theta]$ were get around 240 nm for 3,3'-DBr-BINA(R), 230 nm for BINOL-CH₂(R) and BINOL-POOH(R), and 280 nm for 6,6'-DTPE-BINA(R).

Part II --- Application

According to our previous conclusion, we have synthesized the polymers P-1 and P-2. Although BINOL-CH₂(R) hasn't prevented the CD signal from decaying totally, once forming the polymer, the restraint would increase. So we hoped P-2 could stop the trend of AACD.

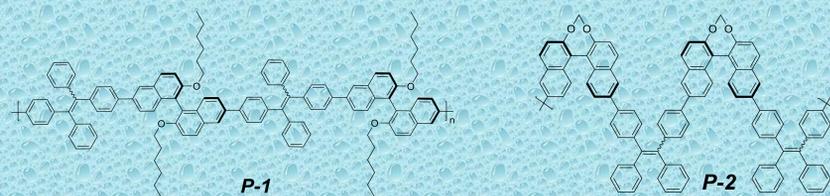


Figure 4 told us P-1 was an AACD polymer, but P-2 was not, whose CD signal hasn't severely attenuated after aggregation. It proved our theory was reliable. Then we tested the CD and CPL performances for P-1 and P-2 respectively, and it was inspiring that we have detected both CD and CPL signal from the film of P-2.

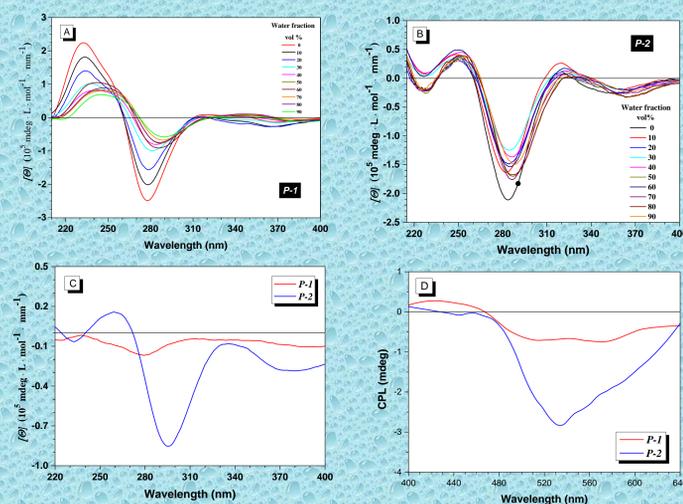


Figure 4. CD spectra of polymers A) P-1 and B) P-2 in different water fraction (THF/H₂O, $c = 10^{-4}$ M); C) CD and D) Circularly Polarized luminescence (CPL) to P-1 and P-2 in the film state.

Conclusion

We have discovered the phenomenon of AACD in the compound 6,6'-DTPE-BINA(R). According to our further research, we have realized it was caused by the change of twist angle between two naphthalene rings. Then we designed and synthesized the polymer P-2, which locked the two rings through a methylene. The results showed us that P-2 not only prevented the CD signal from decreasing during aggregation, but had excellent CD and CPL performances in the film state. It was a new strategy to prepare the chiroptical materials.

References

- J.Z. Liu, H.M. Su, L.M. Meng, Kam S. Wong, B.Z. Tang, et al. *Chem. Sci.* **2012**, 3, 2737.
- H.K. Li, J. Cheng, Y.H. Zhao, W. Y. Lam, S. Wong, H.K. Wu, B.S. Li, B. Z. Tang. *Mater. Horiz.*, **2014**, 1, 518.
- C.Y. Ng, H.K. Li, Q. Yuan, J.Z. Liu, C.H. Liu, X.L. Fan, B.S. Li, B. Z. Tang. *J. Mater. Chem. C.*, **2014**, 2, 4615.