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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis is mainly focused on two parts. In the first part, the synthesis, structures, and photophysical properties of several kinds of cyclophenylene-ethynylenes (CPEs) were disclosed. In the second part, I disclosed the use of the CPEs to the synthesis of corresponding cycloparaphenylene-triphenylenes (CPPTs); the special photophysical properties, aggregation-induced emission (AIE), was observed in all examples, which revealed that this type of cycloparaphenylene (CPP) derivatives is a new class of AIE-active luminogens.

In chapter 1, I disclosed the general overviews of CPPs and CPEs. The replacement of *para*-conjugated benzenes to *ortho*-conjugated biphenyl units introduces the axial chirality into the CPPs. However, these two *ortho*-benzenes on the biphenyl unit significantly increase the steric hindrance. Thus, I designed the CPEs, in which two benzenes are replaced with two acetylenes. Another challenge of synthesizing these nanorings is to overcome the strain energy caused by the largely strained structures. The previous strategies, for example, the reductive, oxidative, and dehydrative aromatization, and the transition-metal complexes, were suffered from problems such as low product yields during the strain-induced steps, being difficult to prepare the starting material, or hard to introduce substituents into the CPPs. Therefore, an alternative strategy: using CPEs as starting material in the synthesis of CPPTs is crucial to overcome the aforementioned problems. Moreover, the axial chiral biphenyl unit shortens the distance between the two active acetylenes compared to other strategies (for example, the [2+2+2] cycloaddition of tetrayne-macrocycles reported by the Wegner group), which makes the cycloaromatization more easily. Additionally, these chiral CPEs presented unique photophysical and chiroptical properties which were disclosed in the next chapter.

In chapter 2, highly curved single [7]CPEs and the figure-eight double CPE with stable axial/ helical chirality were synthesized via double- or tetra-Sonogashira coupling of a U-shaped prearomatic paraphenylene diiodide building block with terminal diynes and tetrayne, respectively, followed by reductive aromatization. Notably, the synthesis of double CPE required $Pd(PPh_3)_4$ instead of $Pd(PPh_3)_2Cl_2$ as catalyst. The replacing of ortho-linked benzenes with acetylenes next to the biphenyl spacers reduced the steric hindrance while remaining stable axial and helical chirality, which were verified by chiral HPLC separation. Moreover, the X-ray analyses of these CPEs revealed that the curvatures on the edge of the paraphenylene moiety were close to the [5]CPP, which cause red-shifted emission. The replacement of a twisted biphenyl spacer into a planar naphthyl spacer removed the hidden writhe so that the Hückel-type CPE turned into a Möbius-type CPE. This CPE was obtained by the same strategy using silyl-protected U-shaped building block and naphthyl diyne as starting materials. The naphthalene-CPE exhibited unique properties due to its Möbius topology which reflected with a similar fluorescence λ_{max} with those smaller-sized [7]CPEs and a much higher fluorescence quantum yields than those [7]CPEs. Based on these results, the larger-sized [9]CPEs were obtained by the same strategy, exhibiting blue-shifted emission and better stabilities compared to those [7]CPEs and the figure-eight double [7]CPE. Moreover, the biphenyle-substituted [9]CPE was used as the starting material of the [2+2+2] cycloaddition in the next chapter.

In chapter 3, a direct synthesis of [8]CPPTs via the cationic Rh(I)/ ligand complexes-catalyzed intermolecular [2+2+2] cycloaddition of the biphenyle-substituted [9]CPE with monoynes was disclosed. The reversed synthetic route was applied to this synthesis as an alternative strategy to prevent the Rh(I)-catalyzed 1,2-aryl rearrangement during the [2+2+2] cycloaddition. These [8]CPPTs presented interesting packing structures due to their intermolecular π-π interactions between benzenes and triphenylene moiety that disclosed by X-ray analyses. Moreover, the dicarboxylate-substituted [8]CPPT could be converted to a highly electron-deficient [8]CPPT with a donor-acceptor system that reflected with a red-shifted fluorescence λ_{max} under powder state. All [8]CPPTs presented the AIE phenomenon that made this type of CPP derivatives become a new class of the macrocyclic AIEgens. Both AIE-active and original photophysical properties of [8]CPP were observed in varying different ratios of THF/ water suspensions. Despite the AIE mechanism of these [8]CPPTs was still ambiguous, the most possible factor could be the largely structural changing during the excited state to reach the minimum energy conical intersection (MECI). The optimized structure of the dicarboxylate-substituted [8]CPPT at excited state done by DFT calculations revealed that the structural distortions exist, which is crucial for reaching the MECI by off-planar distortions.

And the last part is the summary of my all studies of this thesis. In conclusion, the synthesis, structures, and properties of various CPEs including single, double, and the Mobius-type CPEs were disclosed. And based on these results, the use of the biphenyle-substituted [9]CPE and monoynes in the [2+2+2] cycloaddition managed to afford the [8]CPPTs while improved the product yields and avoided the 1,2-aryl rearrangement. The single-crystal X-ray diffraction analyses of the AIE-active [8]CPPTs revealed their highly twisted triphenylene units, which caused the blue-shifted emission and the low quantum yields. And most importantly, these [8]CPPTs are a new class of the AIE-active macrocycle without the TPE moiety that provides a potential application to switchable fluorescence and chemical sensing.