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Editorial

Controlled fluorescent switch based on a cation grease/brake rotor system of pillar[5]arene

In recent years, molecular shuttles, motors, pumps, and elevators, *etc.* could specifically respond external physical or chemical stimuli including light, temperature, pH, redox, solvent and chemical additive to change the structure and function, showing great potential in materials and biological applications [1,2]. Moreover, chirality, as a basic attribution of life systems and nature, has attracted much attention due to its involvement in many biological processes necessary for life. In particular, the reversible regulation of chiral molecules through a variety of stimulus responses has played an increasingly vital role not only in basic science but also in the fields of chiral recognition, asymmetric catalysis, chiral switching, and biological and medical science [3].

Additionally, the rotaxane/catenane assembly shuttles on the axis or rotates around the axis through external stimuli to achieve controllable motion, which is widely used in the construction of molecular machines [4]. Among them, macrocyclic compounds are important components of the rotaxane/catenane wheel especially a class of pillararene with electron-rich cavity columnar structure formed by *para*-linking the benzene ring of hydroquinone with methylene bridge whose unique spatial and chemical structure is more distinctive than other macrocycles, such as (1) excellent host-guest complexation ability; (2) easy to modify and functionalize; (3) unique planar chirality, in which two stable conformers *p*R and *p*S could mutually change through the invertion of the aromatic unit around the methylene bridge. Therefore, this pillararene-based rotor platform and chiral switch have become the focus of researches [5–9].

Yang *et al.* reported the pillararene universal joints with chiral conversion response to ion, temperature, pressure, redox and light (Fig. 1a) [10]. Liu *et al.* also made some progress in the construction of a single-molecule chiral stepping motor by combining dibromo-P5 with tetrathiofuvalene (TTF) derivatives possessing reversible double-electron oxidation-reducing properties (Fig. 1b). With the continuous oxidation of TTF, the conformation of P5-TTF gradually changes to self-inclusion, and the circular dichroism signals gradually change from positive to negative. When reducing agents are added, that the chirality was reversed back to the original state and reversibly switched [11].

Recently, Juli Jiang, Chen Lin, Jing Ma and Leyong Wang from Nanjing University jointly investigated the rotational motion and the kinetic control of pillar[5]arene (P5), and found for the first time that the counter cation has crucial influence on the rotational barrier of the hydroquinone ring in the rotational energy barrier of the anionic P5 (WP5) (Fig. 1c) [12]. With the increase of the ionic radius from Li^+ to Cs^+, the rotational barrier gradually decreases. Owing to the cation-π and hydrogen bond interactions, WP5-NH_4 has the lowest rotational energy barrier that the hydroquinone part rotated fastest whereas WP5-Li the slowest. More importantly, pillararene presented aggregation-induced emission (AIE) properties, so the rotation speed of the hydroquinone part could be changed by cation exchange to achieve the regulation of the luminescence properties, which is applied in fluorescent switches and anti-counterfeiting inks.

Generally, sodium carboxylate P5 and ammonium carboxylate P5 (Fig. 1c) show no appreciable differences in the assembly process. However, Jiang *et al.* found that the ^{1}H NMR signals of methylene at the edge of the two compounds are quite different, where those of WP5-Na split into two doublets but those of WP5-NH_4 a singlet (Fig. 1d). The different counterions made the hydroquinone ring of WP5 equip different rotational barriers, leading to the slower rotation of the hydroquinone ring part in WP5-Na and faster rotation in WP5-NH_4. In addition, various counterionic P5s were also prepared through the reaction of carboxylated P5 (P5-COOH) with the hydroxides of alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+). A close comparison demonstrated that the ^{1}H NMR signals of the methylenes at the edge of WP5-Li, WP5-Na, WP5-K, WP5-Rb and WP5-Cs all split into two bimodal peaks due to the slow rotation, while only WP5-NH_4 with the singlet peak for the fast rotation. The variable-temperature NMR experiments showed that the dimethylene peaks of WP5-Li, WP5-Na, WP5-K, WP5-Rb and WP5-Cs tended to aggregate at 343 K, 338 K, 333 K, 333 K and 328 K, respectively, and the rotation barrier ($\Delta G^{\neq}$) decreases from 18.23 kcal/mol to 15.06 kcal/mol, qualitatively supposed that WP5-NH_4 has the lowest rotation barrier, that is, the fastest rotation speed. According to the size matching effect, the cations with larger size, especially NH_4^+, generated stronger force and the lower rotational barrier, owing to the additional hydrogen bonds between NH_4^+ and carboxylate oxygen.

Subsequently, the binding constants (K_a) of ethoxycarbonylmethoxy-substituted P5 (P5-COOEt) with K^+, Rb^+ and NH_4^+ were measured as $(4.2 \pm 1.3) \times 10^2$, $(7.9 \pm 1.2) \times 10^2$ and $(1.1 \pm 0.1) \times 10^3$ L/mol. In addition, Stoddart's TS model was used to evaluate the energy barriers of TS_1 and TS_2 during rotation (Fig. 1e). The results of potential energy surface scanning (PESS) showed that: (1) the influence of cations on the transition state is greater than that on the ground state, and WP5-Li has the highest rotational barrier for TS_1; (2) due to steric hindrance, the rotational barrier of TS_2a is higher than that of TS_2b, and

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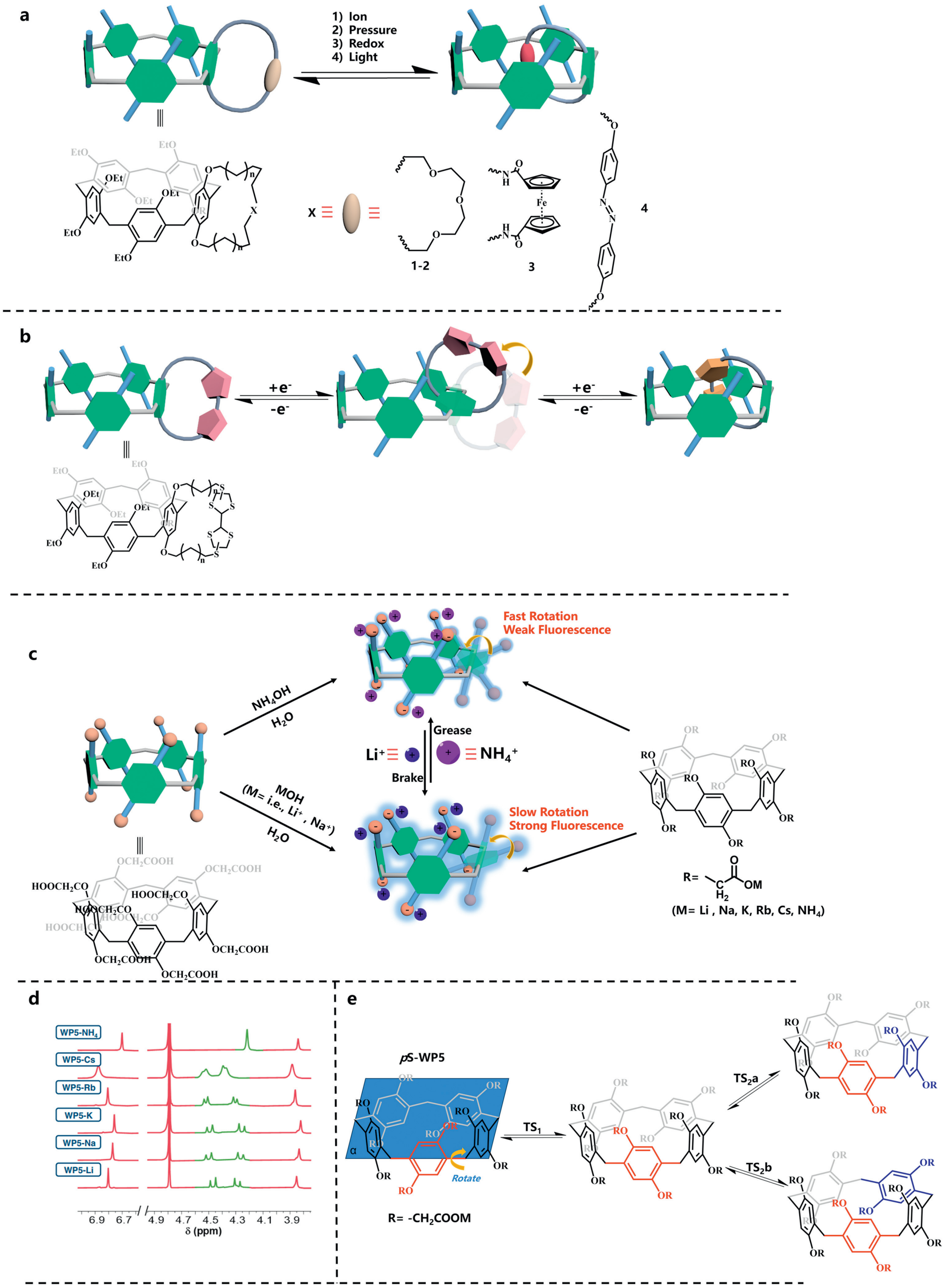

Fig. 1. Scheme illustration of (a) multistimulus-responsive rotary motion; (b) single-molecule chiral stepping motor through double-electron oxidation-reducing; (c) cation-controlled rotary motion of WP5-M; (d) ^{1}H NMR spectra of WP5-M in D_2O (298 K) and (e) conversion pathways of *p*S and *p*R in WP5-M.

the barriers in the two rotational processes (TS_1 and TS_2b) are significantly reduced from WP5-Li, WP5-Na, WP5-K to WP5-NH_4; (3) when the hydroquinone ring is rotated to the plane α, the non-bond distance between the given cation and the M-position vertical phenol ring gradually decreases from WP5-Li to WP5-NH_4, revealing an enhanced cation-π interaction.

The difference in rotation speed of hydroquinone rings in WP5 under different counterions could be applied in constructing cationic grease/brake molecular motors, which were converted to each other for many times due to NH_4^+ and Li^+/Na^+ exchange. Taking the advantages of AIE properties of the pillararene and the cation-controlled WP5-M rotor, the fluorescence intensity decreased with the reduction of the rotational barrier under UV irradiation at 365 nm, and the reversible switch of multiple writing to erasing of the pre-written fluorescent character "7" was achieved through the exchange of Li^+ and NH_4^+.

In conclusion, molecular rotor with controlled motion have become one of the current research hotspots due to their potential applications in functional materials. As a new class of macrocyclic arenes, pillararene not only has a unique plane chirality but also realizes the mutual conversion of two stable conformational isomers through the hydroquinone ring rotation. In the process of building molecular machines based on P5, although a variety of stimulus response modes including solvent, ion, pH, temperature, pressure, redox and light have been developed, the development of new response modes, new systems, new functions and their applications still face great challenges. Jiang's work on constructing an original molecular rotor based on P5 in water system presented that counter cations with different radii affect the rotational barrier of hydroquinone units in WP5, thus affected the rotational velocity, leading to the increased cation-π interaction between cations and electron rich holes with the enhancement of cation radii. Attributing to the cation-π interaction as well as the additional hydrogen bond interaction, hydroquinone ring in WP5-NH_4 rotated with the fastest speed while WP5-Li with the slowest speed. Combined with AIE properties, fluorescence could be erased and read by continuous Li^+-NH_4^+ cationic exchange. We believe that this cation-driven molecular rotor of pillararene in water phase could be used as environmentally friendly intelligent anti-counterfeit ink or biosensor. This study not only broadens the scope of application of cylindrical aromatic molecular rotors, but also provides a broader prospect for the application of molecular machines in smart materials and biomedicine fields.

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References

[1] E. Moulin, L. Faour, C. Carmona-Vargas, et al., Adv. Mater. 32 (2020) 1906036.
[2] Q. Wang, D. Chen, H. Tian, Sci. China Chem. 61 (2018) 1261–1273.
[3] T. Zhao, J. Han, P. Duan, et al., Acc. Chem. Res. 53 (2020) 1279–1292.
[4] C.J. Bruns, J.F. Stoddart, Acc. Chem. Res. 47 (2014) 2186–2199.
[5] W. Yang, W. Zhang, J. Chen, et al., Chin. Chem. Lett. (2023), doi:10.1016/j.cclet.2023.108740.
[6] Li Z, Y.W. Yang, Acc. Mater. Res. 2 (2021) 292–305.
[7] W.L. Zhou, X.Y. Dai, W. Lin, et al., Chem. Sci. 14 (2023) 6457–6466.
[8] C. Shi, H. Li, X. Shi, et al., Chin. Chem. Lett. 33 (2022) 3613–3622.
[9] T. Zhao, W. Wu, C. Yang, Chem. Commun. 59 (2023) 11469–11483.
[10] F. Gao, X. Yu, L. Liu, et al., Chin. Chem. Lett. 34 (2023) 107558.
[11] Y. Sun, L. Liu, L. Jiang, et al., J. Am. Chem. Soc. 145 (2023) 16711–16717.
[12] H. Zheng, L. Fu, R. Wang, et al., Nat. Commun. 14 (2023) 590.