Highly Efficient Förster Resonance Energy Transfer Modulations of Dual-AIEgens between a Tetraphenylethylene Donor and a Merocyanine Acceptor in Photo-Switchable [2]Rotaxanes and Reversible Photo-Patterning Applications

Pham Quoc Nhien,
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

Tu Thi Kim Cuc,
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

Trang Manh Khang,
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

Chia-Hua Wu,
Department of Chemistry, University of Houston, Houston, Texas 77204, United States

Bui Thi Buu Hue,
Department of Chemistry, College of Natural Sciences, Can Tho University, Can Tho City 94000, Viet Nam

Judy I. Wu,
Department of Chemistry, University of Houston, Houston, Texas 77204, United States

Brad W. Mansel,
Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

Hsin-Lung Chen,
Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

Hong-Cheu Lin
Department of Materials Science and Engineering and Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 300, Taiwan

Corresponding Author Phone: +886-3-5723803-55305; linhc@mail.nctu.edu.tw.
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ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c12726. Experimental details and additional data including $^1$H NMR, $^{13}$C NMR, 2D TOCSY NMR, HRMS-ESI, elemental analysis (EA), UV/visible spectra, fluorescence spectra, and DFT calculations (PDF)
Abstract

A series of novel photo-switchable [2]rotaxanes (i.e., Rot-A-SP and Rot-B-SP before and after shuttling controlled by acid–base, respectively) containing one spiropyran (SP) unit (as a photochromic stopper) on the axle and two tetraphenylethylene (TPE) units on the macrocycle were synthesized via click reaction. Upon UV/visible light exposure, both mono-fluorophoric rotaxanes Rot-A-SP and Rot-B-SP with the closed form (i.e., non-emissive SP unit) could be transformed into the open form (i.e., red-emissive merocyanine (MC) unit) to acquire their respective bi-fluorophoric Rot-A-MC and Rot-B-MC reversibly. The aggregation-induced emission (AIE) properties of bi-fluorophoric TPE combined with MC AIEgens of these designed rotaxanes and mixtures in semi-aqueous solutions induced interesting ratiometric photoluminescence (PL) and Förster resonance energy transfer (FRET) behaviors, which were further investigated and verified by dynamic light scattering (DLS), X-ray diffraction (XRD), and time-resolved photoluminescence (TRPL) measurements along with theoretical studies. Accordingly, in contrast to the model axle (Axle-MC) and the analogous mixture (Mixture-MC, containing the axle and macrocycle components in a 1:1 molar ratio), more efficient FRET behaviors and stronger red PL emissions were obtained from dual-AIEgens between a blue-emissive TPE donor (PL emission at 468 nm) and a red-emissive MC acceptor (PL emission at 668 nm) in both novel photo-switchable [2]rotaxanes Rot-A-MC and Rot-B-MC under various external modulations, including water content, UV/Vis irradiation, pH value, and temperature. Furthermore, the reversible fluorescent photo-patterning applications of Rot-A-SP in a powder form and a solid film with excellent photochromic and fluorescent behaviors are first investigated in this report.

Graphical Abstract

Keywords

aggregation-induced emission (AIE); Förster resonance energy transfer (FRET); photo-switchable [2]rotaxane; spiropyran; tetraphenylethylene
1. INTRODUCTION

Featured by the 2016 Nobel Prize in Chemistry, mechanically interlocked molecules (MIMs) are conspicuous archetypes for the development of molecular switches and molecular machines due to the controllable and switchable capabilities of noncovalent interactions between macrocycles and axles to alter their relative positions under different external stimuli. Various kinds of external stimuli, for example, pH, light, redox, and cation binding, have been employed to control the molecular shuttling processes of MIMs in supramolecular chemistry. Therefore, rotaxanes, catenanes, necklaces, and molecular knots belong to the large range of MIMs that have played critical roles to construct responsive materials for the application of molecular sensors, actuators, machines, and smart materials.

The rotaxane is one of the major prototype of MIMs, comprising one (or more) macrocyclic host(s) trapped into the threaded molecule(s) by terminal stoppers, which have attracted more attention because of their unique molecular structures. A variety of rotaxanes have been developed with highly structural complexity by self-sorting, template synthesis, or dynamic combinatorial chemistry and showed extensive applications in various fields, such as chemosensors, mechanical materials, drug delivery, nanotechnology, and biotechnology.

Recently, fluorescent molecular switches (FMSs), which respond to various triggers, including light, force, heat, acid/base, etc., were widely examined due to their broad applications in sensing chemicals, physical parameters, and bioimaging. However, traditional fluorophores normally experience aggregation-caused quenching (ACQ) effects owing to strong π-π interactions of excimers in solid states or concentrated solutions. To overtake the ACQ effect, Tang’s group first discovered the phenomena of aggregation-induced emission (AIE) in 2001. Due to the restricted intramolecular rotation mechanism (RIR), AIE fluorophores display strong emissions in their aggregated states, but they exhibit very weak or no emission in solution. Besides 1-methyl-1,2,3,4,5-pentaphenylsilole, tetraphenylethylene (TPE) is well-known as an AIE luminogen with interesting AIE properties in the aggregation and solid states; so, TPE-based materials are broadly utilized for various practical applications, including multicolor emission materials, pH sensors, fluorescent bioprobes, and chemosensors in aqueous (or semi-aqueous) solutions.

In addition, photochromic and mechanochromic molecules that endure the structural reversibility between two different isomeric structures have garnered a lot of attention due to their interesting properties and applications in photo- and mechano-switchable molecular materials. Spiropyrans and their derivatives are one of the most usually investigated photochromic compounds, which reveal distinct absorption and emission properties as a result of the reversible structural isomerization process between the ring-closed spiropyran (SP) and ring-opened merocyanine (MC) forms under various stimuli, such as UV/visible light, acid–base, heat, and mechanical force. Hence, SP and its analogues have been used for some practical applications, including photo-patterning, anti-counterfeiting inks, secret writings, and rewritable displays. With the advantages of Förster resonance energy transfer (FRET), different combinations of FRET processes between fluorophoric donors and acceptors in a molecule, a supramolecular system, and a...
mixture\textsuperscript{45} have been reported. For example, some FRET systems based on either TPE donors\textsuperscript{46,47} or MC acceptors\textsuperscript{48,49} especially the combination of bi-fluorophoric TPE and SP moieties in organic or polymeric molecules\textsuperscript{50,51} were designed and reported in recent years.

To date, numerous fluorescent supramolecular molecules have been successfully generated by the combination of organic fluorophores (including AIE-active and photochromic fluorophores) via different noncovalent interactions, for example, multiple hydrogen bonds, π-π stacking interactions, charge transfer interactions, electrostatic interactions, and so forth.\textsuperscript{52} It is very intriguing that these supramolecules completely integrate the intrinsic fluorescence properties of fluorogens and the vast stimulus responsivity originated from the noncovalent interactions of supramolecular molecules.\textsuperscript{53–58} Therefore, a number of host-guest systems, including pseudo-rotaxanes and rotaxanes with AIE behaviors,\textsuperscript{59–61} photo-switchable properties,\textsuperscript{56,62,63} and FRET phenomena\textsuperscript{61,64,65} have been reported so far.

Regardless of various designed MIMs with one or two of the abovementioned behaviors, the combination of these three interesting properties of AIE, photo-switchable, and FRET behaviors in a single MIM is also essential to improve their typical responsivities as well as their applications, which warrants the exploration of novel photoluminescence (PL) properties of the MIM molecule in this study. Herein, we design and synthesize a novel photo-switchable [2]rotaxane (i.e., Rot-A-SP) consisting of two AIEgens (TPE and MC moieties) after UV exposure, where TPE is a typical AIE molecule in semi-aqueous solutions or in solids, and SP as a photochromic moiety can undergo photo-isomerization to produce the MC form with AIE phenomena upon UV exposure. The photo-controllable AIE properties, FRET behaviors, pH, and temperature effects of the novel [2]rotaxanes will be investigated by the PL, dynamic light scattering (DLS), and time-resolved photoluminescence (TRPL) spectra in semi-aqueous solutions under reversible responses of UV and visible light exposure. Finally, the excellent photo-switchable properties of Rot-A-SP in a powder form and a solid film are further investigated and utilized as photochromic and fluorescent inks on cellulosic papers for the applications of reversible photo-patterning.

2. EXPERIMENTAL SECTION

2.1. Materials.

All chemical reagents were purchased from commercial sources (Sigma-Aldrich, J. T. Baker, and TCI Japan) and used directly as received without further purification. Some certain solvents used for specific reactions were purified/dried by a solvent purification system before using. All reactions were performed under nitrogen gas with vacuum-line manipulations. Some catalysts, reactants, and organic solvents were used for reactions and purification of compounds, such as tetra-n-butylammonium bromide (TBAB), tosyl chloride (TsCl), disodium ethylenediaminetetraacetate (Na\textsubscript{2}EDTA), triethylamine (TEA), tetrahydrofuran (THF), acetonitrile (ACN), ethyl acetate (EtOAc), methanol (MeOH), dichloromethane (DCM), and hexane (Hex).
2.2. Characterizations and Measurements.

Bruker Advance 300 and 500 MHz instruments were used to measure the nuclear magnetic resonance (NMR) spectra of all compounds at room temperature. The molecular weights of all target compounds were recorded on a Bruker Impact HD mass spectrometer (ESI mode) to obtain the high-resolution mass spectra (HRMS). The elemental analyses were carried out by an Elementar Vario CUBE (CHN-OS Rapid, Germany) instrument. The morphology of compounds was studied on a cold field emission scanning electron microscope (SEM SU8010). The average sizes of all target compounds were determined by a dynamic light scattering (DLS) technique on a DelsaNano C particle analyzer (BECKMAN COULTER). An ultraviolet/visible near-infrared spectrophotometer (Lambda 950, PerkinElmer) between 200 and 800 nm was used to measure absorbance spectra of all compounds. The photoluminescence spectra were recorded with a fluorescence spectrophotometer (HITACHI F-4500). The time-resolved photoluminescence (TRPL) spectra were obtained by a PDL 200 pulsed diode laser.

2.3. Energy Transfer Efficiency Calculation.

Based on the fluorescence lifetime of the donor shown in Table 1, we have calculated the energy transfer efficiency (FRET efficiency, \(E_{\text{FRET}}\)) of Rot-A-MC and Rot-B-MC by the following formula: \(E = 1 - \frac{\tau_{\text{DA}}}{\tau_{\text{D}}}\)

where \(\tau_{\text{d}}\) and \(\tau_{\text{da}}\) represent the donor’s fluorescence lifetime before and after UV exposure, respectively.

2.4. Synthesis and Characterization.

The detailed synthetic procedures and characterization of compounds 1–10, host TPE-Cy-TPE, guest C10-NH\(_2\)+, and stopper SP-N\(_3\) are reported in the Supporting Information (section 1). The synthetic approach of [2]rotaxane 11, Rot-A-SP, and Axle-SP are given here.

2.4.1. Synthesis of [2]Rotaxane 11.—Guest C10-NH\(_2\)+ (735 mg, 1.0 mmol) was dissolved in dry and degassed DCM (25 mL); then, crown ether TPE-Cy-TPE (1.32 g, 1.1 mmol) was added and stirred for 2 h under nitrogen gas. The resulting solution became clear, and [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) (385 mg, 1.0 mmol) was added. After 10 min, the solution of SP-N\(_3\) (566 mg, 1.5 mmol) in dry DCM (20 mL) was injected to the reaction mixture and continuously stirred at room temperature overnight. The mixture was diluted with DCM (20 mL), washed with aqueous Na\(_2\)EDTA 0.1 M solution (2 × 50 mL), saturated aqueous solution of NH\(_4\)PF\(_6\) (2 × 20 mL), and water. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and evaporated to dryness. The crude product was further purified by silica gel column chromatography with a mixed solvent (DCM/MeOH = 50:1) to afford [2]rotaxane 11 as a pale yellow solid (1.46 g, 63.2% yield). \(^1\)H NMR (300 MHz, CD\(_3\)CN, δ ppm): 7.95–7.93 (m, 2H), 7.79 (s, 1H), 7.62 (dd, \(J = 1.5\) Hz, \(J = 8.4\) Hz, 2H), 7.43–7.42 (m, 4H), 7.23 (d,
J = 8.4 Hz, 2H), 7.14–6.99 (m, 37H), 6.95–6.91 (m, 4H), 6.88–6.84 (m, 5H), 6.80–6.77 (m, 2H), 6.66–6.58 (m, 7H), 5.06 (s, 2H), 4.93 (d, J = 10.5 Hz, 1H), 4.75–4.65 (m, 2H), 4.58–4.50 (m, 4H), 4.52 (s, 3H), 4.12–4.05 (m, 8H), 3.88–3.82 (m, 10H), 3.73 (t, J = 6.6 Hz, 2H), 3.65–3.63 (m, 8H), 3.60 (s, 6H), 3.55 (s, 3H), 3.53–3.52 (m, 2H), 1.70–1.56 (m, 4H), 1.40–1.23 (m, 12H), 1.13 (s, 3H), 0.93 (s, 3H).

$^{13}$C NMR (125 MHz, CD$_3$CN, δ ppm): 165.8, 161.1, 160.6, 155.1, 154.7, 153.8, 153.4, 151.1, 148.7, 147.9, 145.2, 145.1, 145.0, 143.1, 142.9, 142.7, 141.7, 137.6, 133.5, 132.5, 132.4, 129.4, 129.3, 128.2, 128.1, 123.5, 122.7, 120.4, 118.9, 117.3, 116.9, 115.9, 108.2, 72.3, 72.2, 72.1, 71.6, 71.4, 70.0, 69.9, 69.7, 69.3, 63.3, 61.4, 60.5, 57.2, 53.9, 50.3, 45.8, 30.8, 30.6, 30.4, 27.4, 27.2. HRMS (ESI$^+$) [M-PF$_6$]$^+$: calcd. for C$_{134}$H$_{135}$N$_{6}$O$_{21}$, 2164.9708; found, 2164.9899.

2.4.2. Synthesis of [2]Rotaxane Rot-A-SP.—In a sealed tube, the solution of [2]rotaxane 11 (1.0 g, 0.43 mmol) in ACN (10 mL) and CH$_3$I (5 mL) was heated at 40 °C for 2 days. The reaction mixture was cooled to room temperature, and the ACN and CH$_3$I excess were then evaporated in vacuum. The solid was washed with ethyl ether twice and then suspended in 20 mL of acetone followed by adding an excessive saturated aqueous solution of NH$_4$PF$_6$, and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure; then, the solid was added with 50 mL of deionized water, filtered, and washed with water (3 × 50 mL). The precipitate was continuously washed with pentane and dried under vacuum for 24 h to give the desired [2]rotaxane Rot-A-SP as a pale yellow solid (1.03 g, 96%).

$^1$H NMR (300 MHz, CD$_3$CN, δ ppm): 8.37 (s, 1H), 8.06–7.95 (m, 2H), 7.64 (dd, J = 1.8 Hz, J = 8.7 Hz, 2H), 7.45–7.42 (m, 4H), 7.24 (d, J = 8.7 Hz, 2H), 7.19–7.02 (m, 37H), 6.97–6.92 (m, 7H), 6.88–6.85 (m, 5H), 6.70 (d, J = 9.0 Hz, 1H), 6.63–6.59 (m, 5H), 5.33 (d, J = 10.2 Hz, 1H), 5.23 (s, 2H), 4.73–4.68 (m, 4H), 4.58–4.50 (m, 2H), 4.23 (s, 3H), 4.18–4.07 (m, 8H), 3.91–3.66 (m, 22H), 3.60 (s, 6H), 3.55 (s, 3H), 1.75–1.62 (m, 4H), 1.42–1.28 (m, 12H), 1.21 (s, 3H), 1.04 (s, 3H). $^{13}$C NMR (125 MHz, CD$_3$CN, δ ppm): 166.4, 165.9, 159.6, 154.0, 153.9, 152.7, 151.1, 149.1, 145.2, 145.1, 143.2, 142.9, 141.8, 134.6, 133.6, 132.5, 132.4, 130.9, 130.6, 129.5, 129.4, 129.3, 128.3, 128.2, 127.7, 125.8, 124.2, 123.4, 122.8, 122.7, 118.9, 117.1, 117.0, 115.8, 114.5, 113.4, 108.8, 72.8, 72.4, 71.5, 71.4, 70.6, 70.2, 69.9, 69.4, 60.5, 55.9, 55.2, 53.7, 49.8, 41.1, 35.2, 30.6, 30.4, 28.3, 27.2, 27.1, 26.8, 25.8, 21.6, 20.7. HRMS (ESI$^+$) [M-2PF$_6$]$^{2+}$: calcd. for C$_{135}$H$_{138}$N$_{6}$O$_{21}$P$_2$F$_{12}$, C 65.63, H 5.63, N 3.40%; found, C 65.18, H 5.53, N 3.65%.

2.4.3. Synthesis of Axle-SP.—Methyl iodide (CH$_3$I, 5 mL) was added to the solution of compound 10 (500 mg, 0.45 mmol) in ACN (10 mL) then heated at 40 °C in a sealed tube for 24 h. Excessive ACN and CH$_3$I were then removed under reduced pressure, and the solid was suspended in 20 mL of acetone. An excessive saturated aqueous solution of NH$_4$PF$_6$, and the mixture was stirred overnight at room temperature. The solvent removed in vacuum led to a residue; then, it was added with deionized water (50 mL), filtered, and washed with water (3 × 50 mL). The precipitate was continuously washed with pentane and dried under vacuum for 24 h to give the desired Axle-SP as a pale yellow solid (521 mg, 91%).

$^1$H NMR (300 MHz, CD$_3$CN, δ ppm): 8.39 (s, 1H), 8.07–7.98 (m, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.19–7.14 (m, 2H), 6.99–6.90 (m, 5H), 6.89–6.86 (m, 3H), 6.74–6.69 (m, 3H), 6.63 (d, J = 7.8 Hz, 1H), 5.33 (d, J = 10.5 Hz, 1H), 5.24 (s, 2H), 4.77–4.74 (m, 2H), 4.24 (s, 3H),
4.13 (d, J = 8.1 Hz, 2H), 3.99–3.89 (m, 5H), 3.83–3.82 (m, 7H), 3.76–3.68 (m, 5H), 1.74–
1.69 (m, 4H), 1.42–1.26 (m, 12H), 1.21 (s, 3H), 1.04 (s, 3H). \(^{13}\)C NMR (125 MHz, CD\(_3\)CN,
\(\delta\) ppm): 162.1, 161.8, 160.4, 156.3, 155.4, 155.2, 152.5, 147.5, 143.1, 141.9, 137.8, 134.5,
133.5, 131.8, 130.6, 129.6, 127.7, 127.5, 124.5, 122.4, 121.9, 120.4, 119.0, 117.9, 117.2, 117.1,
116.6, 116.4, 109.9, 109.0, 108.5, 107.9, 69.9, 69.7, 69.6, 61.6, 61.5, 61.4, 60.9, 60.4, 57.5, 57.4,
54.5, 53.9, 52.8, 52.3, 44.9, 40.2, 40.1, 30.9, 30.8, 30.7, 30.6, 30.5, 27.4, 27.3, 26.7, 20.7. HRMS (ESI\(^{+}\)) [M-2PF\(_6\)]\(^{2+}\): calcd. for C\(_{57}\)H\(_{70}\)N\(_{6}\)O\(_{9}\)2+, 491.2597; found, 491.2598.

3. RESULTS AND DISCUSSION

3.1. Design and Synthesis of Photo-Switchable [2]-Rotaxane and Axle.

Photo-switchable [2]rotaxane Rot-A-SP was synthesized in the presence of a
[Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) catalyst via the “click” reaction (CuAAC) of guest C\(_{10}\)-NH\(_2\) with an
SP-N\(_{3}\) stopper in DCM as AIE macrocycle host TPE-Cy-TPE was trapped at the
ammonium station under a mild condition (Scheme 1). Intermediate [2]rotaxane 11 was
prepared as shown in Scheme 1 followed by the methylation of a triazole group with CH\(_3\)I in
acetonitrile, and the counterion was exchanged with saturated aqueous solutions of NH\(_4\)PF\(_6\)
in acetone. Then, the silica gel flash column chromatography was carried out to obtain
[2]rotaxane Rot-A-SP as a pale yellow solid with a high yield of 60.7% for these 3 steps.
The photo-isomerization of Rot-A-SP was performed under UV irradiation to yield Rot-A-
MC (see Scheme 1). Moreover, the axle of [2]rotaxane, Axle-SP, was also synthesized with
a similar synthetic route of Rot-A-SP without TPE-Cy-TPE. The detailed synthetic
procedures and characterizations of all intermediates and new compounds are described in
the Supporting Information.

3.2. Mechanically Interlocked and Molecular Shuttle of Photo-Switchable [2]Rotaxane.

As shown in Figure 1, the partial \(^1\)H NMR spectra of TPE-Cy-TPE, Rot-A-SP, and Axle-
SP were analyzed and compared to confirm the successful synthesis of [2]rotaxane Rot-A-
SP. Indeed, we observed the obvious downfield shifts of resonance for H\(_4\) and H\(_5\) from 4.13
to 4.68 ppm and from 3.99 to 4.58 ppm, respectively (Figure 1b and c), which are adjacent
to the NH\(_2\)+ group. Besides, the downfield shifts of proton signals H\(_1\), H\(_2\), and H\(_3\) (\(\Delta\delta\)H\(_1\) =
0.15, \(\Delta\delta\)H\(_2\) = 0.23, and \(\Delta\delta\)H\(_3\) = 0.15 ppm) were clearly recognized in Figure 1b and c.
Meanwhile, the proton signals of aromatic protons H\(_{40}\) and H\(_{41}\) were shifted upfield with
\(\Delta\delta\)H\(_{40}\) = 0.08 ppm and \(\Delta\delta\)H\(_{41}\) = 0.18 ppm (see Figure 1a and b). These results reveal that
the ammonium group was threaded by the crown ether unit of TPE-Cy-TPE leading to the
formation of mechanically interlocked molecule Rot-A-SP. In addition, it was noteworthy
that the proton signals of the ammonium ion (NH\(_2\)+) were detected at 7.45 ppm in Rot-A-SP
(Figure 1b) due to the strong hydrogen-bonding interactions between the ammonium
hydrogen atoms on the guest and the oxygen atoms on crown ether of the host, whereas the
Axle-SP could not be observed in Figure 1c. Based on these analyses of \(^1\)H NMR spectra,
HRMS, and EA results, we can conclude that [2]rotaxane Rot-A-SP was successfully
synthesized by a mechanically interlocked molecule method via the formation of hydrogen
bonding.
It is widely known that crown ether has a stronger binding ability toward the secondary ammonium unit than the N-methyltriazolium unit;\textsuperscript{56} so, TPE-Cy-TPE sits on the ammonium salt station initially (Figure 2a). Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and trifluoroacetic acid (TFA) were used as external stimuli in [2]rotaxane Rot-A-SP to study the shuttling motion of macrocycle TPE-Cy-TPE on Axle-SP. The highly reversible shuttling behavior between [2]rotaxanes Rot-A-SP and Rot-B-SP under respective acid and base conditions was confirmed by the comparison of \textsuperscript{1}H NMR spectra in Figure 2. Upon the addition of 1 equiv. of DBU, the initial Rot-A-SP solution in CD\textsubscript{3}CN was transformed into Rot-B-SP, where significant downfield shifts of triazolium proton H\textsubscript{22} from 8.37 to 9.25 ppm (\(\Delta\delta\textsubscript{H} = 0.88\) ppm) along with minor downfield shifts of \(\Delta\delta\textsubscript{H} = 0.22\) ppm and \(\Delta\delta\textsubscript{H} = 0.27\) ppm were observed (see Figure 2a and b). On the other hand, the resonance of protons H\textsubscript{4}, H\textsubscript{5}, and H\textsubscript{21} in the N-methyltriazolium unit was obviously shifted upfield with respective values of \(\Delta\delta = 0.58, 0.68,\) and 0.46 ppm. Additionally, the disappearance of the proton signal at 7.45 ppm was also observed in Figure 2b due to the deprotonation of a secondary ammonium salt by DBU addition. These \textsuperscript{1}H NMR shifts clearly imply that TPE-Cy-TPE moved from ammonium to triazolium station by the complexation of the macrocycle with the triazolium ring under the base condition. However, upon the addition of 2 equiv. of TFA, the protonation of the NH group in Rot-B-SP occurred to lead shuttling back of macrocycle TPE-Cy-TPE to the original station (ammonium recognition site) and transforming back to initial Rot-A-SP, which is proven by the re-emergence of all proton signals (H\textsubscript{4}, H\textsubscript{5}, H\textsubscript{6}, H\textsubscript{21}, H\textsubscript{23}, and NH\textsubscript{2}+) in the \textsuperscript{1}H NMR spectrum (Figure 2c). Therefore, macrocycle TPE-Cy-TPE might be slipped between two stations (ammonium and N-methyltriazolium recognition sites in Rot-A-SP and Rot-B-SP, respectively), indicating reversible shuttling behavior of this [2]rotaxane upon acid–base stimuli (Figure 2d).

### 3.3. AIE Behaviors of Rot-A-SP and Rot-B-SP.

With successful shuttling behaviors of [2]rotaxanes Rot-A-SP and Rot-B-SP in acidic and base conditions, respectively, we further examined their AIE properties in the THF/H\textsubscript{2}O system with different water fractions by their photoluminescence (PL) experiments (with a suitable excitation wavelength of \(\lambda\textsuperscript{ex} = 365\) nm absorbed by all of our compounds in this study, and their UV/visible spectra are shown in Figure S30a,b). As shown in Figure 3a and Figure S31a, both [2]rotaxanes Rot-A-SP and Rot-B-SP were non-emissive in pure and concentrated THF solutions (H\textsubscript{2}O \(\leq 60\%\)) due to intramolecular rotations of TPE units, resulting in consuming the excited state energy non-radiatively.\textsuperscript{67} As the water fraction increased over 70% in THF/ H\textsubscript{2}O solutions, due to the high polarity of water, the spontaneous ring-opening reaction of the SP unit occurred in Rot-A-SP and Rot-B-SP, which was partially transformed into the open form of the MC unit with red emission ca. 650 nm in Figure 3a and Figure S31a by the excitation of a PL machine at \(\lambda\textsuperscript{ex} = 365\) nm. Additionally, as the water fractions increased to 70–90%, we observed gradual enhancements of PL emissions at 468 nm in Rot-A-SP and Rot-B-SP solutions, and they could reach the highest AIE intensities at 90% water (see Figure 3a,b and Figure S31a,b), where the inset figures showed non-emission and strong blue emission in pure THF and 90% water, respectively. However, due to the partial precipitation of non-water-soluble Rot-B-SP in H\textsubscript{2}O/THF solvents (95% H\textsubscript{2}O, v/v), all non-water-soluble rotaxane compounds in further...
studies were prepared and maintained as homogeneous semi-aqueous solutions to reach the maximum amount of water content at 90% H$_2$O (v/v with THF) with the maximum and saturated PL emissions in all major investigations of ratiometric AIE and distinct FRET behaviors. Owing to the restriction of intramolecular motions of TPE units, both Rot-A-SP and Rot-B-SP exhibited almost similar AIE behaviors of TPE in the aggregation state (≤70% H$_2$O) but without any PL contributions from their non-emissive SP units. Besides, the absorption spectra of Rot-A-SP and Rot-B-SP with different water fractions also revealed their interesting aggregation processes in Figure S31c and d. Nonetheless, due to the smaller steric hindrance and an extra positive triazolium charge of Rot-A-SP, it revealed a larger aggregation size of 352.3 nm than that of Rot-B-SP (97.2 nm) in 90% H$_2$O shown in Table 1 and Figure 3c,d, respectively, but both illustrated similar AIE intensities of TPE emissions regardless of their different aggregation sizes. However, a little higher PL quantum yield (1.64%) of Rot-B-SP than that (1.42%) of Rot-A-SP was obtained in Table S1, which was confirmed by the larger aggregation SEM morphology of Rot-B-SP than that of Rot-A-SP shown in Figure S32a and c. In comparison with Rot-A-SP and Rot-B-SP in 90% H$_2$O, the highest AIE intensity of macrocycle TPE-Cy-TPE (see Figure S30d) and the second highest AIE intensity of Mixture-SP (see Figure S31f), which contains both free macrocycle TPE-Cy-TPE and axle Axle-SP (1:1 molar ratio), were observed in the aggregation state (with respective DLS sizes of 243.0 and 172.3 nm in Table 1) owing to the less steric hindrance of non-rotaxane arrangements.

3.4. PL Properties and FRET Behaviors of Rot-A-MC, Rot-B-MC, and Mixture-MC.

As a photochromic fluorophore, the non-emissive SP unit can undergo reversible photo-isomerization from the closed form to its photoluminescent open form of the MC unit under UV/Vis exposure, leading to the reversible conversion of Rot-A-SP to Rot-A-MC (and Rot-B-SP to Rot-B-MC) in Scheme 1. Furthermore, the partial MC absorption band of Rot-B-MC is overlapped with a TPE emission band of Rot-B-SP in Figure S33a, resulting in similar Förster resonance energy transfer (FRET) processes of releasing emission energy from a TPE donor to be absorbed by an MC acceptor in Rot-A-MC, Rot-B-MC, and Mixture-MC. As shown in Figure 4, during the opening processes of SP to MC moieties (from 0 to 90 s after UV exposure) for Rot-A-SP, Rot-B-SP, and Mixture-SP in H$_2$O/THF solvents (90% H$_2$O), the initial TPE donor emissions at 468 nm were gradually decreased, and the newly formed MC acceptor emissions at 668 nm were gradually enhanced to different saturated intensities owing to various FRET behaviors induced by distance-dependent bi-fluorophoric AIEgens (TPE and MC moieties). Accordingly, the inset PL photo-images of Rot-A-MC, Rot-B-MC, and Mixture-MC (in 90% H$_2$O) revealed different extents of FRET and energy transfer (ET) emission color changes (after 90 s of UV exposure) from initial blue to final orange, red, and pink in Figure 4a, c, and e, respectively. Interestingly, Rot-B-MC displayed the largest FRET process with an energy transfer efficiency ($E_{\text{FRET}}$) of 65.6% and the strongest red MC intensity with the reddest emission color in all insets of photo-images, where the shortest FRET distance of a TPE donor and an MC acceptor is demonstrated in Figure 4d. Among them, Rot-A-MC exhibited a medium FRET behavior with $E_{\text{FRET}} = 58.8$%, i.e., larger than Mixture-MC and smaller than Rot-B-MC, due to the middle distance between a donor and an acceptor as shown in Figure 4b.

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Therefore, the corresponding $E_{\text{FRET}}$ values of Rot-A-MC and Rot-B-MC, which include the normalization of different donor energies from their original AIE behavior of the TPE units, are acquired as 58.8 and 65.6%, respectively, revealing that the energy transfer between the TPE and MC moieties of Rot-B-MC is stronger than that of Rot-A-MC. Furthermore, owing to the larger morphological aggregation of Rot-B-SP, the induced larger AIE effect also contributed to the higher PL quantum yield of Rot-B-MC in comparison with RotA-MC. However, Mixture-MC consisting of the mixture of macrocycle TPE-Cy-TPE and axle Axle-MC showed the weakest ET behavior with a slight increase in MC intensity as a pink emission color (see Figure 4e and inset), where the longest distance between a TPE donor and an MC acceptor is illustrated in Figure 4f. Above all, highly efficient FRET processes of both [2]rotaxanes Rot-A-MC and Rot-B-MC were confirmed by the nearly disappeared blue TPE donor emissions at 468 nm, which still existed in Mixture-MC with less effective ET behavior. In addition, based on TRPL measurements, the lifetime values of TPE emissions in the rotaxanes, macrocycle, and mixture are shown in Figure S33b and summarized in Table 1 to further confirm distance-dependent FRET processes between blue TPE and red MC emissions. Regarding the closed form of Rot-A-SP and Rot-B-SP without FRET phenomena, we observed longer lifetime values of a TPE donor at 468 nm with 4.47 and 4.45 ns, respectively, whereas Rot-A-MC and Rot-B-MC showed shorter corresponding lifetime values of 1.84 and 1.53 ns with FRET processes. Moreover, Mixture-MC possessing the least ET process demonstrated the longest lifetime (2.81 ns) of TPE emission due to the longest bi-fluorophoric distance of a TPE donor and an MC acceptor in Figure 4f. Importantly, the most efficient FRET process in Rot-B-MC revealed the shortest lifetime (1.53 ns) of TPE emission, where the schematic illustration of photo-switching behavior between Rot-B-SP and Rot-B-MC via reversible UV/visible exposure is shown in Figure 4d.

The AIE behaviors of bi-fluorophoric Rot-A-MC, Rot-B-MC, and Mixture-MC with coexistence of a blue TPE donor and a red MC acceptor are also investigated by their PL measurements with different water contents and demonstrated in Figure 5a, c, and e, respectively. As illustrated in Figure 5a–f, similar AIE phenomena of gradually enhanced PL intensities were observed in both [2]rotaxanes (Rot-A-MC and Rot-B-MC) and the mixture of the macrocycle and the axle (Mixture-MC) with increased water fractions, and the PL photo-images of Rot-A-MC (orange emission), Rot-B-MC (red emission), and Mixture-MC (pink emission) in 90% H2O are demonstrated in the corresponding insets of Figure 5b, d, and f. Though Rot-A-MC and Rot-B-MC have the same maximum emission wavelength, they exhibit corresponding orange and red emission colors due to different emission peak widths. Hence, the CIE 1931 coordinates of Rot-A-MC and Rot-B-MC originated from their PL data are also demonstrated in Figure S33c, where Rot-A-MC and Rot-B-MC possessed the color coordinates of (0.56, 0.27) and (0.46, 0.24), respectively. As water contents were enhanced from 0 to 60%, the PL intensities of MC acceptor emissions (at 668 nm via FRET attributed to an MC acceptor) in Rot-A-MC, Rot-B-MC, and Mixture-MC were regularly enlarged, and their PL emission bands were blueshifted in Figure 5a, c, and e, respectively. However, redshifts of the PL emission band were observed with high water contents (≥70% H2O). Both hypsochromic and bathochromic shifts of rotaxanes Rot-A-MC and Rot-B-MC in various water fractions can be explained by the MC stacking in two

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different ways shown as follows: (l) H-aggregates yielded from “side-by-side” (antiparallel) arrangement of dipoles lead to blueshifts of PL; (2) “Head-to-tail” (parallel) stacking of dipoles will give J-aggregates to redshifts of PL. Similarly, a larger PL quantum yield (3.12%) of Rot-B-MC than that (2.66%) of Rot-A-MC was obtained in Table S1, which was attributed to the best FRET process of Rot-B-MC along with the larger SEM morphological aggregation of Rot-B-MC than that of Rot-A-MC shown in Figure S32b and d. However, similar SEM morphological aggregations of Rot-A-SP and Rot-A-MC as well as those of Rot-B-SP and Rot-B-MC were observed before and after UV exposure in Figure S32a,b and c,d, respectively. Compared with gradual enhancements of blue TPE emissions ($\lambda_{em} = 468$ nm) at high water contents ($\geq 60\%$ H$_2$O) in mono-fluorophoric rotaxanes (Rot-A-SP and Rot-B-SP) and Mixture-SP (see Figure 3a,b and Figure S31a–f), the bi-fluorophoric Rot-A-MC, Rot-B-MC, and Mixture-MC exhibited increased AIE behaviors of red MC emissions ca. 625–668 nm, which started at pure THF ($\geq 0\%$ H$_2$O) (see Figure 5b, d, and f). In comparison with bi-fluorophoric rotaxanes (Rot-A-MC and Rot-B-MC), Mixture-MC displayed weaker red MC emissions at low water contents ($<60\%$ H$_2$O, before the occurrence of ET processes originated from the TPE donor), which was similar to that of Axle-MC shown in Figure S30e with initially enhanced and finally decreased PL intensities by increasing water fractions (reaching a maximum PL ca. 50–60% H$_2$O) in Figure S30f. Thus, the more confined and bulky design of rotaxanes in bi-fluorophoric Rot-A-MC and Rot-B-MC induced stronger AIE behaviors of red MC emissions than Axle-MC and Mixture-MC at low water contents ($<60\%$ H$_2$O, without FRET processes). Furthermore, the gradually decreased MC emissions of Axle-MC at high water contents ($\geq 60\%$ H$_2$O) in Figure S30f did not happen in bi-fluorophoric rotaxanes (Rot-A-MC and Rot-B-MC) and Mixture-MC, where the AIE behaviors of MC continued to enhance red emission intensities in Figure 5b, d, and f due to the support of FRET processes originated from the TPE donor. Moreover, the TPE donor emission in Figure 5e could be observed in Mixture-MC due to its weaker ET behavior, which induced the pink PL emission at 90% H$_2$O in the inset of Figure 5f. Nevertheless, little blue TPE emissions in Figure 5a,c could be perceived in both rotaxanes (Rot-A-MC and Rot-B-MC) due to their efficient FRET behaviors in comparison with Mixture-MC. The continuously increased red MC emission properties induced by FRET behaviors of Rot-A-MC and Rot-B-MC at high water contents were verified by the decreased red MC emissions of Axle-MC at high water contents ($>60\%$ H$_2$O) in Figure S30f. Surprisingly, the combination of the bi-fluorophoric rotaxane design in Rot-A-MC and Rot-B-MC can contribute such huge enhancements of red MC emissions via FRET processes in contrast to pure Axle-MC (or Mixture-MC) excited with a fixed wavelength at 365 nm.

The aggregation distributions of Rot-A-MC and Rot-B-MC with the average sizes of 305.7 and 100.9 nm (shown in Figure S35a and b, respectively) were confirmed by DLS measurements, which suggest that the larger aggregation size of Rot-A-MC was due to its lower steric hindrance and an extra positive triazolium charge. The aggregation states of Rot-A-SP (352.3 nm), Rot-B-SP (97.2 nm), Rot-A-MC (305.7 nm), and Rot-B-MC (100.9 nm) were further surveyed by small-angle X-ray scattering (SAXS) measurements, which are shown in Figure S36a,b, and their model fitting parameters are summarized in Table S2. Interestingly, the larger sizes of Rot-A-SP (352.3 nm) and Rot-A-MC (305.7 nm) before
shuttling along with smaller sizes of Rot-B-SP (97.2 nm) and Rot-B-MC (100.9 nm) after shuttling were estimated to be matchable with fitting vesicle and sphere packing models, respectively. Compared with rotaxanes Rot-A-MC and Rot-B-MC, Mixture-MC possessed the weakest AIE behavior and the worst ET phenomenon to show a pink emission color, which are demonstrated in Figure 5e and f, regardless of its medium average size of 150.8 nm (Figure S35f and Table 1).

3.5. pH Effects on FRET Behavior.

According to our previous report, the PL emissions of MC moieties under various pH conditions illustrated different FRET behaviors due to the protonation and deprotonation of MC moieties. Herein, we investigate the pH effects on PL emissions of Axle-MC, Mixture-MC, Rot-A-MC, and Rot-B-MC in semi-aqueous (90% H$_2$O) solutions. Axle-MC in the open form reveals weak PL emissions and pH-responsive photo-physical properties in Figure S37a,b, where the PL intensities of Axle-MC are gradually decreased from the neutral to acidic conditions (pH = 1–6) and significantly quenched in all base conditions (pH = 8–13) in Figure S37b. More interestingly, the PL emissions of both rotaxanes Rot-A-MC and Rot-B-MC were almost stable to have an MC emission at 668 nm in neutral and acidic media (except Rot-A-MC at pH =1) and slightly decreased at high pH values (pH = 9–13) with approximately 42 and 27% reduction of PL intensities for Rot-A-MC and Rot-B-MC, respectively (Figures 6a,b and c,d), leading to minor PL emission color changes in the insets of these figures. Furthermore, the pH effects (pH = 1, 7, and 13) on the absorbance of Rot-A-MC and Rot-B-MC were observed with the decreased absorption intensities ca. 530–600 nm in acidic (pH =1) and basic (pH = 13) conditions in contrast to the neutral condition. Regarding Rot-A-MC at pH = 1, a new absorption peak occurred at 430 nm, indicating the protonation of the MC unit to form Rot-A-MCH$^+$, which resulted in the reduced absorbance at 547 nm (Figure S37c) and decreased PL intensity at 668 nm (Figure 6a). In the basic condition (pH = 13), both shuttling switching and partial MC isomerization might occur at the same time to reduce the absorbance and PL intensity of Rot-A-MC. However, Rot-B-MC (after shuttling) exhibited a slight pH-dependent effect with more stable absorbance and PL intensity than that of Rot-A-MC (see Figure S37d and Figure 6d), which may be attributed to the steric hindrance of TPE-Cy-TPE nearby the MC unit in Rot-B-MC, leading to the diminished protonation of the MC unit in the acidic condition and restricted MC isomerization. In contrast, Mixture-MC exhibited distinct PL emission color changes in the pH range of 1–13 due to the relative PL intensity changes of TPE and MC moieties (Figure 6e,f). The emission intensity of TPE at 468 nm was gradually enhanced, and the emission intensity of MC ca. 650 nm was slightly decreased with the pH value reduced from 7 to 1 (Figure 6f), in which the emission colors of Mixture-MC changed from red to white in this low pH range below 7 (inset of Figure 6f). However, the PL intensities of MC were suddenly decreased under higher pH values (pH = 9–13), leading to a strong greenish blue emission at pH = 13 as shown in insets of Figure 6f. In contrast to rotaxanes Rot-A-MC and Rot-B-MC, much stronger blue PL emissions of TPE in all pH ranges (pH = 1–13) observed in Figure 6f could be evidenced by the weaker ET behavior in Mixture-MC due to the longer distance between the energy donor (TPE-Cy-TPE) and acceptor (Axle-MC). Owing to the close distance of a TPE donor and an MC acceptor attached to the macrocycle and the
stopper of the axle, respectively. Rot-A-MC and Rot-B-MC demonstrate their more efficient and stable FRET behavior to possess much weaker blue TPE donor and stronger red MC acceptor emissions in these rotaxane systems than those of Mixture-MC in all pH ranges (pH = 1–13).

3.6. Temperature Effects on FRET Behavior.

Besides UV/Vis exposure and acid–base conditions, we have noticed that SP can also undergo the isomerization between closed and open forms by temperature variations. Therefore, the temperature-dependent FRET processes of Rot-A-MC, Rot-B-MC, and Mixture-MC were examined upon heating from 20 to 60 °C and are shown in Figure 7. The PL intensities at 668 nm (MC emission) and 468 nm (TPE emission) of both rotaxanes Rot-A-MC and Rot-B-MC were gradually decreased and increased, respectively, in the range of 25–50 °C due to the conversion from Rot-A-MC to Rot-A-SP and from Rot-B-MC to Rot-B-SP, leading to the elimination of FRET phenomena (Figure 7a–d), where the PL photo-images are shown in the insets of Figure 7b,d. Additionally, the SP forms of Rot-A-SP and Rot-B-SP were recovered by respective heating of Rot-A-MC and Rot-B-MC up to 60 °C, which could be also studied by their absorption spectra with a disappearance of their absorption bands around 530–550 nm in Figure S38c and d, respectively. In comparison, both Axle-MC and Mixture-MC in Figure S38b and Figure 7f exhibited diminished MC emission upon heating to 45 °C (see Figure S38a and Figure 7e) because of the thermal isomerization of MC moieties from their red-emissive open form to non-emissive closed form. In addition, the blue TPE emission of Mixture-MC was recovered and enhanced during this heating process as a result of ET reduction, where the PL emission colors of their photo-images are shown in the insets of Figure 7f. Accordingly, these results reveal that FRET processes of Rot-A-MC, Rot-B-MC, and Mixture-MC can be adjusted by changing temperature in the range of 25–60 °C owing to the isomerization between non-emissive SP and red-emissive MC forms. Thus, due to their rotaxane structural effect, the MC red emissions in both rotaxanes Rot-A-MC and Rot-B-MC could still be partially maintained in the open form up to the high temperature range at 40–60 °C in contrast to Axle-MC and Mixture-MC. Overall, the more stable MC form and highly efficient FRET at various temperatures obtained in the rotaxane design of Rot-A-MC and Rot-B-MC than those of Axle-MC and Mixture-MC can be verified by the temperature effects on their red MC emissions at 25–60 °C.

3.7. Theoretical Calculations.

To investigate the FRET switching mechanism, the theoretical calculations were performed for six compounds Rot-A-SP, Rot-B-SP, Rot-A-MC, Rot-B-MC, Axle-SP, and Axle-MC at a B3LYP/6–31G(d) method in the gas phase. The absorption spectra of these compounds were computed using the time-dependent density functional theory (TD-DFT) approach68 at the same level of theory. All calculations were performed using Gaussian 16 program.69 The central-central distances between TPE and MC were 2.9–4.1 nm in Rot-A-MC and 1.1–1.7 nm in Rot-B-MC (Figure 8a and b), within the range of required donor-acceptor distance (1–10 nm) for the FRET process.40 The additional strong absorption at ~500 nm was found in the compounds containing the open form of MC (Rot-A-MC, Rot-B-MC, and Axle-MC,
Table 2), corresponding to the excitation on the MC motif. Therefore, the FRET process from TPE emission ($\lambda_{\text{max}} = 468 \text{ nm}$) to MC absorption is effective. However, the $\sim 500 \text{ nm}$ absorption peak was absent for the compounds containing the closed forms (Rot-A-SP, Rot-B-SP, and Axle-SP, Table 2), and the FRET did not occur. The orbital energy gap of MC in the corresponding electronic transition (Table 2, Figure 8c, and Figure 9) was generally smaller than that of SP. For the $\sim 500 \text{ nm}$ absorption peak at the MC unit of Rot-A-MC and Rot-B-MC, the orbital energy gaps were 2.70 eV (HOMO-4 $\rightarrow$ LUMO) and 2.69 eV (HOMO-2 $\rightarrow$ LUMO), respectively. The same orbital energy gaps for the SP unit of Rot-A-SP and Rot-B-SP (Table 2 and Figures S42 and S43) were 5.04 or 4.96 eV (HOMO-25 $\rightarrow$ LUMO+1 or HOMO-9 $\rightarrow$ LUMO+3) and 5.01 eV (HOMO-5 $\rightarrow$ LUMO+5). Therefore, the absorption at the SP unit was only $\sim 270 \text{ nm}$ for Rot-A-SP and Rot-B-SP. In addition, the LUMO energy of a TPE donor was significantly higher than an MC acceptor in Rot-A-MC (LUMO+3 was 1.72 eV higher than LUMO, Figure 8c) and Rot-B-MC (LUMO+3 was 1.33 eV higher than LUMO, Figure 9) but close or even lower in energy than an SP acceptor in Rot-A-SP (LUMO+2 was 0.57 eV higher than LUMO+1 but 0.12 eV lower than LUMO+3, Figure S42) and Rot-B-SP (LUMO+1 was 0.59 eV lower than LUMO+5, Figure S43). These results indicate that the FRET processes occurred at the open form of both rotaxanes Rot-A-MC and Rot-B-MC in semi-aqueous solutions, where Rot-B-MC exhibited a higher FRET efficiency than that of Rot-A-MC with approximately 25% enhanced intensity (see Figure 4a,c) due to a closer distance (1.1–1.7 nm) of Rot-B-MC between a TPE donor and an MC acceptor.

3.8. Photo-Switchable FRET Behaviors and Reversible Photo-Patterning Applications of Rot-A-SP in a Solid Film.

With highly efficient FRET processes of our designed [2]rotaxanes Rot-A-MC and Rot-B-MC (after shuttling in base conditions) in the THF/H$_2$O solutions (90% water fraction), herein, we further investigated the photochromic and fluorescence properties of Rot-A-SP (rather than Rot-B-SP treated in solution) in a powder form and a thin solid film, which was blended with poly(methyl methacrylate) (PMMA). As shown in Figure 10a, Rot-A-SP exhibited slight yellow and strong blue-green photoluminescence under visible light exposure in a powder form, which would be changed to Rot-A-MC after UV or sunlight exposure to show deep blue and strong red photoluminescence due to the energy transfer from a TPE donor to an MC acceptor via the FRET process. Similarly, the coated cellulosic paper of Rot-A-SP with excellent photochromic and fluorescent behaviors exhibited a white color and strong blue PL emission, which could be converted to a purple color and strong red PL emission, respectively, after UV or sunlight exposure (Figure 10b). Both the powder form and coated paper of Rot-A-SP showed good FRET ON–OFF behaviors due to the reversible photo-isomerization between SP and MC forms under respective UV/sunlight and Vis/heating conditions. In addition, the transparent PMMA film of Rot-A-SP (0.5 wt %) was fabricated by drop-casting of a viscous solution (which was prepared from the homogeneous dispersion of Rot-A-SP in THF solution) on a Petri plate and left for drying at room temperature. Significantly, this solid film displayed multiemission colors from strong blue, violet, pink, and reddish pink to strong red under various UV exposure times, as illustrated in Figure 10c. Based on these results, Rot-A-SP in a powder form, coated cellulosic paper,
and solid film could be utilized for practical applications, including photo-switchable materials, smart devices, and ink. Therefore, Rot-A-SP can be utilized as photochromic and fluorescent inks on paper in order to observe different emission colors via FRET phenomena. As displayed in Figure 10d, the characters of “TPE SP”, “TPE MC”, FRET on”, and “FRET off” were handwritten on the cellulosic papers from the solution of Rot-A-SP; then, solvent was evaporated by heating to obtain the initial white papers with strong blue emissions of “TPE SP”, “TPE MC”, and “FRET off” characters. Upon various UV/sunlight exposure times, these letterings displayed multimission colors (strong blue, opaque pink, pink, and strong red); meanwhile, the initial colorless “TPE SP” and “TPE MC” characters were turned to purple by naked-eye observation (Figure 10d), indicating the presence of FRET phenomena. As stimulus-responsive papers, blue emissions of characters on these handwriting samples would be recovered under visible light or heating treatment due to the re-closed ring of the SP unit leading to shut down FRET processes. These results indicate that our designed photo-switchable [2]rotaxanes could be utilized for interesting and practical applications, such as rewritable inks, secret writings, lithography, reversible photo-patterning, and anti-counterfeiting materials for display technologies.

4. CONCLUSIONS

In summary, we have synthesized and developed a series of novel FRET [2]rotaxanes with a spiropyran (SP) stopper and a TPE-based macrocycle, i.e., Rot-A-SP and Rot-B-SP (before and after shuttling), where the SP unit can be transformed into the photo-isomeric merocyanine (MC) unit by UV irradiation to achieve bi-fluorophoric Rot-A-MC and Rot-B-MC, respectively. The reversible Förster resonance energy transfer (FRET) ON/OFF behaviors of the TPE donor and MC/SP moieties upon respective UV/visible light exposure were investigated in semi-aqueous solutions. Upon UV exposure, the ratiometric PL of FRET-ON processes between dual-AIEgens of a TPE donor and an MC acceptor were acquired in both Rot-A-MC and Rot-B-MC, where Rot-B-MC produced a stronger red emission of the energy acceptor (i.e., MC unit) with a higher FRET efficiency ($E_{\text{FRET}}$) of 65.6% than that ($E_{\text{FRET}} = 58.8\%$) of Rot-A-MC due to the shorter distance of fluorophoric TPE and MC moieties after shuttling. However, before UV exposure or upon visible light exposure, the blue emission energy of TPE at 468 nm in mono-fluorophoric Rot-A-SP and Rot-B-SP could not be transferred to the non-emissive SP stopper in the FRET-OFF state. The combination of dual-AIEgens (i.e., TPE donor and MC acceptor) in both Rot-A-MC and Rot-B-MC offered more prominent and continuously enhanced AIE and FRET-ON properties by increasing water contents in contrast to the model axle (Axle-MC) and the analogous mixture (Mixture-MC). Additionally, the pH effects on the isomeric MC form of all novel compounds were also reported, in which Rot-A-MC and Rot-B-MC revealed more enhanced red MC emission at 668 nm than that of Mixture-MC in the range of pH = 1–13. Moreover, by temperature variations, the more stable open form of MC and highly efficient FRET phenomena could be obtained in both Rot-A-MC and Rot-B-MC up to a high temperature range (at 40–60 °C) in contrast to Axle-MC and Mixture-MC. In general, the novel dual-AIEgens demonstrate the more efficient and stable FRET processes between TPE donor and MC acceptor moieties in the well-designed photo-switchable [2]-rotaxanes under different external modulations, including water contents, UV/Vis exposure, acid–base...
conditions, or temperature variations. Owing to the interesting FRET phenomena, Rot-A-SP displayed excellent photochromic and fluorescent behaviors in a powder form and a solid film under UV/sunlight and Vis/heating processes, which have been successfully employed in distinct and reversible fluorescent photo-patterning applications. We believe that this report may contribute to facile and efficient FRET design of smart photo-switchable fluorescent materials for future potential applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Partial $^1$H NMR spectra (300 MHz, 298 K, CD$_3$CN) of (a) TPE-Cy-TPE, (b) Rot-A-SP, and (c) Axle-SP.
Figure 2.
Partial $^1$H NMR spectra (300 MHz, 298 K, CD$_3$CN) of (a) Rot-A-SP, (b) deprotonation of Rot-A-SP with 1 equiv. of DBU, (c) reprotonation of Rot-A-SP with 2 equiv. of TFA, and (d) mechanically interlocked and shuttling motion of AIE photo-switchable [2]rotaxane under acid/base conditions.
Figure 3.
(a) PL spectra and (b) relative emission intensities of Rot-A-SP (50 μM) vs different water fractions and DLS results of (c) Rot-A-SP and (d) Rot-B-SP in H₂O/THF solvents (90% H₂O, v/v). (insets) Fluorescence photo-images of Rot-A-SP solutions in pure THF (left) and H₂O/THF (90% H₂O, v/v) (right) solvents under a UV lamp, λ<sub>ex</sub> of 365 nm and λ<sub>em</sub> of 468 nm.
Figure 4.
Time-dependent PL spectra of (a) Rot-A-SP, (c) Rot-B-SP, and (e) Mixture-SP in H$_2$O/THF solvents (90% H$_2$O, v/v) upon UV exposure (0–90 s) and schematic illustrations of energy transfer (ET) processes from TPE to MC units of (b) Rot-A-SP, (d) Rot-B-SP, and (f) Mixture-SP via ET processes after UV exposure. (insets) Photo-images of photoluminescence color changes (after 90 s of UV exposure). Concentration of 50 μM and $\lambda_{ex}$ of 365 nm.
Figure 5. PL spectra and relative emission intensities of (a,b) Rot-A-MC, (c,d) Rot-B-MC, and (e,f) Mixture-MC vs different water fractions. (insets) Fluorescence photo-images of (b) Rot-A-MC, (d) Rot-B-MC, and (f) Mixture-MC in pure THF (left) and H₂O/THF (90% H₂O, v/v) (right) under a UV lamp. Concentration of 50 µM and λ<sub>ex</sub> of 365 nm.
Figure 6.
PL spectra and relative PL intensities of (a,b) Rot-A-MC, (c,d) Rot-B-MC, and (e,f) Mixture-MC in H₂O/THF solvent (90% H₂O, v/v) at various pH values. (insets) PL photo-images of (b) Rot-A-MC, (d) Rot-B-MC, and (f) Mixture-MC at different pH values. Concentration of 50 μM and λ<sub>ex</sub> of 365 nm.
Figure 7.
PL spectra and relative PL intensities of (a,b) Rot-A-MC, (c,d) Rot-B-MC, and (e,f) Mixture-MC in H₂O/THF solvent (90% H₂O, v/v) at various temperatures (20–60 °C). (insets) PL photo-images of (b) Rot-A-MC, (d) Rot-B-MC, and (f) Mixture-MC at different temperatures. Concentration of 50 μM and λ<sub>ex</sub> of 365 nm.
Figure 8.
Optimized structures of (a) Rot-A-MC and (b) Rot-B-MC and (c) molecular orbital energies of MC and TPE units in Rot-A-MC involved in the electronic transition. See the Supporting Information for the full list of absorptions.
Figure 9.
Molecular orbital energies of MC and TPE units in Rot-B-MC involved in the electronic transition. See the Supporting Information for the full list of absorptions.
Figure 10.
Photo-images of Rot-A-SP in (a) powder form (top: naked-eye and bottom: PL observation) and (b) coated cellulosic papers (top: naked-eye and bottom: PL observation) under UV/sunlight and Vis/heating processes, (c) PL emission color changes of a PMMA film blended with Rot-A-SP (0.5 wt %) under various UV exposure times, and (d) photo-patterning features of photochromic and multicolor fluorescent inks based on Rot-A-SP under UV/sunlight and Vis/heating processes.
Scheme 1.
Synthetic Routes for Axle-SP, Rot-A-SP, Rot-A-MC, Rot-B-SP, and Rot-B-MC
Table 1.

Average Sizes ($d$, nm) and Lifetime Values ($\tau$, ns) of Rot-A-SP, Rot-A-MC, Rot-B-SP, Rot-B-MC, Axle-SP, Axle-MC, TPE-Cy-TPE, Mixture-SP, and Mixture-MC<sup>a</sup>

| compound       | Rot-A-SP | Rot-A-MC | Rot-B-SP | Rot-B-MC | Axle-SP | Axle-MC | TPE-Cy-TPE | Mixture-SP | Mixture-MC |
|----------------|----------|----------|----------|----------|---------|---------|------------|------------|------------|
| $d$(nm)<sup>b</sup> | 352.3    | 305.7    | 97.2     | 100.9    | 21.6    | 40.2    | 243.0      | 172.3      | 150.8      |
| $\tau$(ns)<sup>c</sup> | 4.47     | 1.84     | 4.45     | 1.53     |         |         | 6.16       | 6.05       | 2.81       |

<sup>a</sup>Measured in THF/H<sub>2</sub>O solutions (90% H<sub>2</sub>O).

<sup>b</sup>Determined by DLS.

<sup>c</sup>Determined by TRPL at $\lambda$<sub>ex</sub> of 365 nm and $\lambda$<sub>em</sub> of 468 nm.
Table 2.
Absorption Spectra Computed at TD-B3LYP/6–31G(d)

| compounds | λ (oscillator strength) | major electronic transition                           |
|-----------|-------------------------|--------------------------------------------------------|
| Axle-SP   | 271 (0.26)              | HOMO-8 → LUMO (43%)                                    |
|           |                         | HOMO-6 → LUMO+2 (42%)                                   |
| Axle-MC   | 497 (0.51)              | HOMO-1 → LUMO (96%)                                    |
|           | 384 (0.30)              | HOMO-5 → LUMO (82%)                                    |
| Rot-A-SP  | 268 (0.43)              | HOMO-25 → LUMO+1 (50%)                                 |
|           |                         | HOMO-9 → LUMO+3 (36%)                                  |
| Rot-B-SP  | 271 (0.20)              | HOMO-5 → LUMO+5 (46%)                                  |
| Rot-A-MC  | 497 (0.51)              | HOMO-4 → LUMO (96%)                                    |
|           | 384 (0.30)              | HOMO-17 → LUMO (82%)                                   |
| Rot-B-MC  | 500 (0.65)              | HOMO-2 → LUMO (98%)                                    |
|           | 377 (0.32)              | HOMO-14 → LUMO (71%)                                   |

*a*Only absorptions involving excitation of the SP/MC units are listed. See the Supporting Information for the full list of absorption peaks. Absorption wavelengths (λ) are given in nm, and only transitions with oscillator strengths (values in parentheses) > 0.2 are listed.