# Nacromolecules Cite This: Macromolecules XXXX, XXX, XXX-XXX

Article

# Porous Organic Polymer from Aggregation-Induced Emission Macrocycle for White-Light Emission

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**Supporting Information** 

ABSTRACT: A tetraphenylethylene-based oxacalixarene macrocycle (TOM) with high fluorescence quantum yield (70%) was used as monomer to construct a fluorescent macrocycle-based porous organic polymer (pTOM). With high surface area, specific pore size, and emissive properties, the blue-greenish fluorescent pTOM can be developed into white-light-emission materials by adsorbing guests of tris-(bipyridine)ruthenium with complementary emission color by the Förster resonance energy transfer (FRET) effect.

# ■ INTRODUCTION

Porous organic polymers (POPs),<sup>1,2</sup> new-generation porous materials with salient advantages including high surface area, low mass density, and high stability, exhibit unique advantages in the field of gas storage, recognition, or catalysis using diverse functional building blocks. Undoubtedly, the property of functional building blocks is considered to be a crucial element to influence the pore performance and potential applications of POPs.<sup>3-11</sup> Supramolecular macrocycles,<sup>12</sup> a kind of artificial macrocyclic compound including rotaxanes,<sup>13</sup> calixarenes,<sup>14</sup> cucurbiturils,<sup>15</sup> pillararenes,<sup>16</sup> and cyclophanes,<sup>17</sup> may be a good candidate for the building block of POPs. Owing to the intrinsic cavities and shape-persistent property, macrocyclic molecules display favorable selectivity toward various kinds of organic guest molecules, which give rise to a considerable increase in research of molecular recognition and self-assembly processes over the past few decades. Recently, several macrocycle-based POPs have been reported,<sup>18-23</sup> utilizing macrocyclic molecules as monomers, which exhibit excellent performance in gas storage, guest recognition, and pollutant separation.

Among various kinds of POPs, the fluorescent POPs not only exhibited unique advantages in gas storage but also possessed potential application in chemosensors and illuminating materials because of their high porosity and strong fluorescence, like conjugated microporous polymers (CMPs).<sup>24-27</sup> However, the  $\pi - \pi$  stacking interactions in CMPs easily trigger the thermal decay of photoexcited states and result in less or no fluorescence because of the aggregation-caused quenching (ACQ) mechanism. To construct fluorescent POPs, utilization of fluorescent monomer with the aggregation-induced emission (AIE) effect might be a promising strategy.<sup>28-34</sup> The POPs, constructed from AIE monomers which were effectively fixed by the



frameworks and cause the radiative decay process to become predominant and emit strong fluorescence, could be a high quality porous fluorescent materials. Moreover, with the property of porosity, the fluorescence of these materials could be tuned through adsorbing appropriate guest dyes, even for the full wavelength white light. However, such materials are rarely reported.

White-light-emission materials have attracted increased interest over the past decade due to their potential applications in display technologies and fluorescent sensors.<sup>35–40</sup> Because of the growing demand for white-light-emission materials in industry, employing organic material instead of the traditional phosphors would be an efficient method to avoid the costly rareearth-containing materials.<sup>41-45</sup> Currently, various organic porous materials explored developed for white-light emission are mainly based on  $\pi$ -conjugated polymers<sup>46</sup> and metalorganic frameworks (MOFs).<sup>44-47</sup> But the  $\pi$ -conjugated polymers easily lost their fluorescence because of the ACQ effect, and the white-light-emission MOFs are usually constructed by rare-earth metals (for example, Eu<sup>3+</sup>, Tb<sup>3+</sup>, and  $Dy^{3+}$ ), which limit their practical application. On the contrary, the AIE-based pure organic POPs, exhibiting strong fluorescence in the solid state without containing rare-earth metal, would be promising materials for illumination. Up to now, one of the most exploited strategies to develop white-light-emission materials is carefully tuning of partial Förster resonance energy transfer (FRET) between the donor-acceptor chromo-phores.<sup>46,51,52</sup> To obtain a bicomponent white-light-emission

Received: July 30, 2018 Revised: September 16, 2018 Scheme 1. Graphical Representation of Synthesis of TOM and pTOM



energy transfer system, the colors of host POPs and guest dyes must be the two complementary colors (for example, blue and orange) in required intensities that cover the visible wavelength range from 400 to 700 nm.<sup>53</sup> Taking advantage of permanent porosity, the POPs can encapsulate suitable guest dyes to form a bicomponent energy donor—acceptor system that exhibits distinct photoluminescent properties which can be easily tuned to various colors by regulating the proportion between the host POPs and the encapsulated guest dyes. Thus, to develop a bicomponent fluorescent POP for energy transfer white-light-emission materials, the key problem is constructing a host POP with specific pore size and emission wavelength which allows the guest dye penetrating into so that the energy transfer could proceed.

Recently, we synthesized a tetraphenylethylene (TPE)-based emissive oxacalixarene macrocycle (TOM) by one-pot nucleophilic aromatic substitution (S<sub>N</sub>Ar) reaction.<sup>54-58</sup> Considering the AIE effect of TPE moiety which exhibits strong fluorescence at wavelength of 480 nm in aggregation state, we predicted that if the TOM is polymerized, the rotation and vibration of phenyl rings in TPE units may be restricted, resulting in an emissive porous framework, and may offer an alternative approach to develop an energy transfer white-lightemission material after adsorbing a specific guest dye. Herein, we synthesized a macrocycle-based polymeric framework (pTOM) by nickel(0)-catalyzed Yamamoto-type Ullmann cross-coupling reaction (Scheme 1).<sup>59,60</sup> The strategy of networking macrocycles by covalent coupling not only overcame the interlaced mode of macrocycles to turn on their pores and displayed significantly enhanced Brunauer-Emmett-Teller (BET) surface area and CO<sub>2</sub> capture capacity compared with that of TOM monomers but also exhibited strong blue-greenish fluorescence.

# EXPERIMENTAL SECTION

General Information. The raw materials of zinc powder, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, TiCl<sub>4</sub>, BBr<sub>3</sub>, benzophenone, 4,4'-dihydroxybenzophenone, 4,4'-dimethoxybenzophenone, 2,3,5,6-tetrachloropyridine, 2,2'-bipyridyl, bis(1,5-cyclooctadiene)nickel, and 1,5-cyclooctadiene were purchased from Aladdin or J&K and used as received. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a DMX600 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. UV spectra were recorded on SHIMADZU UV-2041PC spectrometer. Emission spectra were obtained on a HITACHI F-4500 spectrometer. The X-ray intensity data were collected on a standard Bruker SMART-1000 CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube ( $\lambda = 0.71073$  Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator. The structures were solved by using direct methods and were refined by employing fullmatrix least-squares cycles on F2 (Bruker, SHELXTL-97). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Sample was degassed at 120 °C for 10 h under vacuum before analysis. N2 isotherms were measured at 77 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure. CO2 isotherms were measured at 273 and 298 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure.

Atomistic Simulations. Molecular models were generated from Xray crystallographic data structure using Materials Studio 7.0 (Accelrys). Connolly surfaces were calculated by rolling a probe molecule across the substrate, the interface taken from the contact point of the probe molecule.

**Experimental Details.** Synthesis of 1,1-Bis(4-hydroxyphenyl)-2,2-diphenylethene (1). Benzophenone (1.82 g, 10 mmol), 4,4'-dihydroxybenzophenone (2.14 g, 5 mmol), and zinc powder (5.24 g, 80 mmol) were added to a 250 mL round-bottom flask with THF (100 mL). The mixture was cooled under an ice-water bath, and titanium tetrachloride (4.4 mL, 40 mmol) was added dropwise and then recovered to room temperature and reflux overnight. The reaction was then quenched by 50.0 mL of saturated  $K_2CO_3$  (5.0 M), and the supernatant solution was collected after stirring for 30 min. The organic



Figure 1. (a, b) Fluorescence spectra of TOM in THF after the addition of various amounts of water at the concentration of  $5.0 \times 10^{-6}$  M (excitation wavelength: 310 nm) and variations of fluorescent intensity at 480 nm. (c) Photos under UV irradiation of TOM with water fractions (v/v) in THF/ water mixture.

extracted with DCE and dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1 v/v) as eluent to afford 1 as a white solid in 38% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.17–6.96 (m, 10H), 6.94–6.83 (t, 4H), 6.62–5.51 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 153.3, 143.5, 139.0, 135.9, 132.1, 130.7, 127.0, 126.9, 125.6, 114.0, 113.9.

Synthesis of TOM. 1,1-Bis(4-hydroxyphenyl)-2,2-diphenylethene 1 (400 mg, 1.10 mmol), 2,3,5,6-tetrachloropyridine 2 (238 mg, 1.10 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (1.08 g, 3.30 mmol) were added to a 100 mL round-bottom flask. DMSO (25 mL) was added, and then the combined mixture was stirred vigorously at 120 °C overnight. After the raw materials were consumed, the reaction was allowed to cool to RT; the mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and H<sub>2</sub>O (40 mL) and separated, and the aqueous layer was extracted twice with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The combined organics were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. Products were simply isolated by recrystallized from  $CH_2Cl_2/MeOH$  (220 mg, 40%). <sup>1</sup>H NMR (600 MHz,  $\dot{CDCl}_3$ ):  $\delta$  7.75 (s, 2H), 7.11–7.09 (t, *J* = 12 Hz, 20H), 6.98–6.99 (d, J = 6 Hz, 8H), 6.79–6.80 (d, J = 6 Hz, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 154.28, 151.18, 143.96, 141.77, 141.22, 140.26, 139.28, 132.30, 131.38, 127.89, 126.74, 121.12, 110.55. MALDI-TOF-MS: m/z 1016.3 (M<sup>+</sup>). Anal. Calcd for C<sub>62</sub>H<sub>38</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 73.24; H, 3.77; N, 2.76. Found: C, 73.12; H, 3.95; N, 3.02. Crystallographic data for TOM:  $M_r = 1016.74$ , orthorhombic, space group C2, a = 35.279(5), b = 12.2498(16), c = 12.5944(16) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 94.960^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 5422.4(13) Å<sup>3</sup>, Z = 4,  $\rho_{\text{calcd}} = 1.245 \text{ g/cm}^3$ ,  $\mu = 0.267 \text{ mm}^{-1}$ , reflections collected 20200, data/ restraints/parameters 10114/1/6496, GOF on  $F^2$  1.088, final  $R_1$  = 0.0587,  $wR_2 = 0.1566$ , R indices (all data):  $R_1 = 0.0767$ ,  $wR_2 = 0.1763$ , largest difference peak and hole: 0.994 and -0.251 e/Å<sup>3</sup>, CCDC-1525730.

Synthesis of pTOM. Under a dry argon atmosphere, TOM (250 mg, 0.25 mmol), 2,2'-bipyridyl (230 mg, 1.5 mmol), and bis(1,5-cyclooctadiene)nickel (405 mg, 1.5 mmol) were added to a 100 mL two-neck round-bottom flask, followed by a solution of 1,5-cyclo-octadiene (160 mg, 1.5 mmol) in 30 mL of DMF added by a syringe. The combined mixture was stirred at 85 °C for 5 days before the reaction was allowed to cool to RT. 40 mL of 2 M HCl was added into

the reaction solution and stirred for 0.5 h. The precipitated polymer was collected by filtration and washed with a large amount of water, the products were successively washed with excess THF and  $CH_2Cl_2$  and then sequentially purified by Soxhlet extraction with methanol, and the purified products were dried in a vacuum oven at 60 °C for 12 h to obtain the final pTOM (200 mg, 92%).

## RESULTS AND DISCUSSION

The tetraphenylethylene (TPE)-based emissive oxacalixarene macrocycle TOM was synthesized by one-pot ( $S_NAr$ ) reaction of dihydroxytetraphenylethylene 1 with 2,3,5,6-tetrachloropyridine 2 in the presence of  $Cs_2CO_3$  in DMSO at 120 °C for overnight resulted in the formation of TOM in yields of 40% as depicted in Scheme 1. Products were simply isolated by recrystallized from  $CH_2Cl_2/MeOH$ . The FT-IR, NMR, MALDI-TOF MS, elemental analysis, and X-ray single crystal diffraction analysis were used to characterize the structures of TOM.

The <sup>1</sup>H NMR spectrum of TOM in  $CDCl_3$  (Figure S1) shows one singlet at  $\delta$  = 7.75 ppm for the proton of the pyridine moiety, and the <sup>13</sup>C NMR (Figure S2) shows 13 signals for the different carbons in TOM. The TOM adopts the conformation of the 1,3alternate as only one set of proton and carbon signals were observed, which was further confirmed by X-ray single crystal diffraction analysis as discussed below. With TPE units in their scaffolds, the fluorescent properties of TOM were investigated in solution. As we expected, TOM shows typical AIE properties (Figure 1). It is almost nonfluorescent when excited at  $\lambda = 310$ nm (see Figure S3 for the UV/vis absorption spectrum) in THF (good solvent), but the fluorescent intensity begins to enhance after increasing the fraction (v/v) of water (bad solvent) in THF to 80%. When the fraction of water was increased up to 95%, the solution of TOM showed a strong green fluorescence with a quantum yield ( $\Phi_f$ ) of 70%, which was similar to our precursor TPE-based calixarenes.<sup>61,62</sup>



**Figure 2.** Top view (a) and side view (b) of X-ray crystal structures of TOM. The layered structure formed by the open-chain of TOM (the neighboring open chains of TOM structures were presented by different colors) (c). The cross-sectional images of the packing structures with (d) and without (e) the oxacalixarene framework show that cTOM has nonconnective lattice voids, as illustrated by the gray Connolly surface (probe radius = 1.82 Å) applied to the crystal structure for the desolvated material.



**Figure 3.** (a) <sup>13</sup>C CP-MAS NMR spectrum. (b) TEM image (bar =  $0.2 \mu m$ ). (c) SEM image (bar =  $2 \mu m$ ). (d) Powder X-ray diffraction (PXRD) of pTOM.

The suitable single crystals of TOM for X-ray single crystals analysis were obtained by diffusing Et<sub>2</sub>O into the TOM solution of dichloromethane. Similar to most reported oxacalixarenes, TOM adopts 1,3-alternate conformation in the solid state as shown in Figures 2a and 2b. In the solid state, TOMs formed 1-D infinite open-chain structure by the interaction of C–H… $\pi$  ( $d_{C-H...\pi} = 2.665$  Å) (Figure S4) that are reversely interdigitated to form layered structures (Figure 2c and Figure S5) by



Figure 4.  $N_2$  sorption isotherms of pTOM at 77 K (a), pore size distributions of pTOM calculated using the NLDFT method (b), and CO<sub>2</sub> sorption isotherms of cTOM and pTOM at 273 K (c) and 298 K (d). In (a), (c), and (d), filled symbols denote gas adsorption, and empty symbols denote desorption.

interaction of C-H···Cl ( $d_{H\cdots Cl} = 2.908$  Å,  $\theta_{C-H\cdots Cl} = 161.93^{\circ}$ and 2.868 Å,  $\theta_{C-H\cdots Cl} = 134.36^{\circ}$ ) and  $\pi \cdots \pi$  stacking ( $d_{\pi \cdots \pi} = 2.369$  Å). Moreover, by the virtue of  $\pi \cdots \pi$  stacking ( $d_{\pi \cdots \pi} = 2.330$  Å) and C-H·· $\pi$  ( $d_{C-H\cdots \pi} = 2.893$  Å) (Figure S6), the layered structure was extended into a three-dimensional framework. However, as shown in Scheme 1, the crystalline structure of TOM (cTOM) was a nonporous framework even after removing the solvent because the interlaced mode give rise to the formation of nonconnective lattice voids, which is illustrated by the gray Connolly surface (probe radius = 1.82 Å) (Figures 2d and 2e). The N<sub>2</sub> sorption experiment of cTOM after desolvation at 120 °C for 10 h under vacuum showed no N<sub>2</sub> uptake without significant BET surface area and confirmed the crystallographic measurements and atomistic simulations.

Considering functional groups of chlorine in the outside of the macrocycle which gave a chance to ameliorate the nonporous framework of cTOM, Yamamoto-type Ullmann cross-coupling reactions were used to polymerize the TOM into a novel macrocycle-based emissive porous polymer pTOM (Scheme 1). The amount of Ni residue in pTOM was measured as low as 0.10 wt % by inductively coupled plasma mass spectrometry (ICP-MS). The successful construct of pTOM from monomers TOM was confirmed unambiguously by Fourier transform infrared (FT-IR) analysis and <sup>13</sup>C cross-polarized magic angle spinning solid-state (CP-MAS) NMR spectroscopy. By comparing the FT-IR spectra of TOM and pTOM (Figure S7), the aromatic C-Cl bending vibrations at 1091 cm<sup>-1</sup> disappeared after the monomers were polymerized. Furthermore, the results of <sup>13</sup>C CP-MAS NMR shows that the resonance peaks at  $\delta$  = 156, 141, and 103 ppm can be assigned to the aromatic carbon in the pyridine rings and 152, 141, 139, 130, 126, and 119 ppm for the carbons of for the carbons in the TPE moiety (Figure 3a). From

the results of transmission electron microscopy (TEM) (Figure 3b) and scanning electron microscopy (SEM) (Figure 3c), the pTOM formed rough particles, which further was confirmed by the powder X-ray diffraction (PXRD) experiment that pTOM is noncrystalline (Figure 3d). The thermogravimetric analysis (TGA) showed that pTOM is thermally stable without significant mass loss below 500 °C under a nitrogen atmosphere (Figure S8).

The pTOM was desolvated at 120 °C for 10 h under vacuum before the gas adsorption and desorption properties were investigated. From the results of nitrogen sorption analysis, the Brunauer-Emmett-Teller (BET) surface areas and pore volumes are 268 m<sup>2</sup> g<sup>-1</sup> (the Langmuir surface area is 375 m<sup>2</sup> g<sup>-1</sup>) and 0.273 cm<sup>3</sup> g<sup>-1</sup> for pTOM (Figure S9), which can demonstrate that pTOM formed porous frameworks from nonporous frameworks. As shown in Figure 4a, pTOM showed a steep nitrogen uptake at low relative pressure which implies the presence of macropores in their frameworks. The phenomenon that low-pressure hysteresis is extending to the lowest attainable pressures is associated with the irreversible uptake of gas molecules in the pores (or through pore entrances), which hints at a swelling of the polymer matrix at 77 K by nitrogen. Based on nonlocal density functional theory (NLDFT) (Figure 4b), the pore size distribution was calculated that confirmed the existence of micropores and mesopores in pTOM, which may result from expanded networks.

The CO<sub>2</sub> capture experiments were performed at 273 and 298 K. As shown in Figures 4c and 4d, although the cTOM shows no BET surface area, it can uptake CO<sub>2</sub> 15.4 cm<sup>3</sup> g<sup>-1</sup> at 273 K/1.0 bar and 9.4 cm<sup>3</sup> g<sup>-1</sup> at 298 K/1.0 bar. That can be explained by two reasons: (1) the size of the N<sub>2</sub> molecule (3.64 Å) is larger than the CO<sub>2</sub> molecule (3.3 Å); (2) the electron-rich properties



Figure 5. (a)Fluorescence spectrum of pTOM (black) and absorption spectrum of  $Ru(bpy)_3Cl_2$ . (b) Fluorescence spectra of pTOM. (c) Photos under UV irradiation. (d) CIE chromaticity diagram that shows the luminescent color changes after adding different amounts of  $Ru(bpy)_3Cl_2$ .

of nitrogen and oxygen atoms in pTOM skeleton facilitate localdipole/quadrupole interactions with CO<sub>2</sub> which could be adsorpted on the surface of cTOM, while the pTOM showed much better CO<sub>2</sub> uptake capacities of 33.6 cm<sup>3</sup> g<sup>-1</sup> at 273 K/1.0 bar and 19.6 cm<sup>3</sup> g<sup>-1</sup> at 298 K/1.0 bar. According to the CO<sub>2</sub> adsorption isotherms at 273 and 298 K, the isosteric enthalpy  $(Q_{st})^{63}$  of pTOM for CO<sub>2</sub> was calculated to be 31.5 kJ/mol, which is higher than that of cTOM (23.9 kJ/mol) using the Clausius–Clapeyron equation (Figure S10). The selectivity of CO<sub>2</sub>/N<sub>2</sub> for pTOM was found to be 19, which was calculated from analysis of initial of slopes of the adsorption isotherms by one single gas adsorption experiments at 273 K (Figure S11).

Tris(bipyridine)ruthenium (Ru<sup>2+</sup>) is one of the best standard model luminophores that always has high quantum efficiency in both an aqueous and a nonaqueous medium. It exhibits visiblelight absorption, strong emission, and a long lifetime and is thus widely used as redox photosensitizers for various photoreactions.<sup>64</sup> One application here is obvious: using the pTOM and  $Ru(bpy)_3Cl_2$  as fluorescent donors and receptors to develop a new light-harvesting luminescent material which could potentially generate white-light emission, a property that is of great importance for the lighting industry. There are two prerequisites for the fluorescence resonance energy transfer: (1)As shown in Figure 5a, the excitation wavelength of  $Ru(bpy)_3Cl_2$ overlapped with the emission wavelength of pTOM; (2) the main pore size distribution (11.7 Å) of pTOM is in accordance with the size of  $Ru(bpy)_3^{2+}$  (9.6 Å) (shown in Figure 4b and Figure S12) and the nitrogen atoms on pTOM skeleton facilitated the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> to be adsorbed, leading to the fluorescent donors and acceptor so close to each other. As for the fluorescense property of pTOM, it emitted strong greenishblue fluorescence when dispersed in CH<sub>2</sub>Cl<sub>2</sub> solution upon excitaton at  $\lambda = 365$  nm. After adding various amounts of

 $Ru(bpy)_3Cl_2$  to the solutiong of pTOM (2 mL, 0.25 mg/mL), emission spectroscopy studies revealed that the fluorescent intensity of the Ru(bpy)<sub>3</sub>Cl<sub>2</sub>at 600 nm increased gradually at the expense of the fluorescent intensity of the pTOM at 430 nm (Figure 5b). The fluorescent color changes from greenish blue to orange that can be distinguished by the naked eye illuminated with a UV lamp (excitation wavelength  $\lambda = 365$  nm), which are consistent with the coordinates on the chromaticity diagram (CIE 1931), as shown in Figures 5c and 5d. Of particular interest is the observation that an intense white-light emission solution (CIE coordinates (0.30, 0.33)) is established upon adding  $Ru(bpy)_3Cl_2$  to 35 ppm, which is very close to that of the pure white (0.33, 0.33) light. This white-light emission solution exhibited good stability, which can keep white light without significant variation after being placed for 1 week (Figure S13). The efficiency of energy transfer of white-light emission solution was 60%, which was estimated from the quenching data, using the equation<sup>51,65</sup>

$$E = 1 - \frac{I_{\rm DA}}{I_{\rm D}}$$

where *E* is the fractional energy transfer efficiency,  $I_D$  is the intensity of donor emission in the absence of the acceptor, and  $I_{DA}$  is the intensity of donor emission in the presence of the acceptor. This efficiency is higher than the reported Pan's<sup>42</sup> white-light-emission porous fiber (18.06%) and Jiang's<sup>43</sup> POP white-light-emission films (30%–50%). As the white-light materials are often used in solid state, the luminescence property of the complex pTOM and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> in the solid state has been investigated. After evaporating the CH<sub>2</sub>Cl<sub>2</sub> of white light solution and being grinded into homogeneous powder, the

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complex of pTOM and  $Ru(bpy)_3Cl_2$  can also emit white light in the solid state under UV irradiation (365 nm) (Figure S14).

# CONCLUSIONS

In summary, we have developed a novel emissive polymeric framework (pTOM) based on the oxacalixarene macrocycle (TOM) as monomer. In the solid state, it was found that pTOM overcame the interlocking assembly mode of TOM and performed enhanced porous properties including enhanced BET surface area, pore volume, and  $CO_2$  capture. By the virtue of its strong fluorescence and the macrocycle-based porous framework, pTOM could be used to capture the luminophore of tris(bipyridine)ruthenium (Ru<sup>2+</sup>) to achieve a new white-lightemission material through effective Förster resonance energy transfer. Given the porous properties ameliorative behavior of simple model emissive materials presented here, we envision that further study of intrinsic cavity-based porous polymers will offer not only maintained properties of the monomers such as fluorescent property but also endowed or improved new properties which presented here are to overcome interlocking assembly mode of macrocycles to turn on their pores, which are beneficial for the simultaneous illuminating and gas storage applications.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b01632.

Original data of all the NMR, UV, FT-IR, and X-ray single crystals analysis of TOM, the gas adsorption experiments of pTOM and chemical structure of tris(bipyridine) ruthenium ( $Ru^{2+}$ ) (DOCX)

X-ray crystallographic data of TOM (CIF)

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# Author Contributions

Z.W., S.Y., and H.C.C. contributed equally to this work. **Notes** 

#### notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (21672078 and 21875079), the Natural Science Foundation of Hubei Province (2016CFB372), and the Applied Basic Research Program of Wuhan City (201601010101017). We thank the Analytical and Testing Center of Huazhong University of Science and Technology for related analysis. We also thank Dr. Yao Yu and Wuhan National High Magnetic Field Center for analysis of solid-state NMR.

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