Journal of
Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. Jagadesan, G. Eder and P. Mcgrier, *J. Mater. Chem. C*, 2017, DOI: 10.1039/C7TC00123A.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-c

View Article Online
DOI: 10.1039/C7TC00123A

Journal Name

COMMUNICATION

The Excited-State Intramolecular Proton Transfer Properties of Three Imine-Linked Two-Dimensional Porous Organic Polymers

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

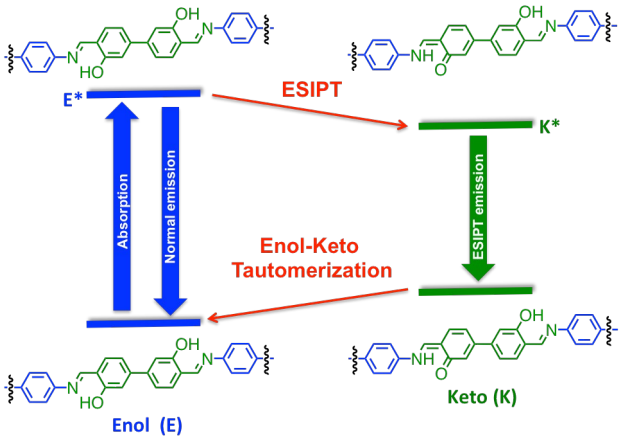
www.rsc.org/

Pradeepkumar Jagadesan, Grace Eder, Psaras L. McGrier*

We report the synthesis and excited-state intramolecular proton transfer (ESIPT) properties of three tris(*N*-salicylideneaniline)-based (TSA) imine-linked porous organic polymers (POPs) containing C_3-symmetric 1,3,5-triarylbenzene (TAB), -tristyrylbenzene (TSB), and -tris(arylethynyl)benzene (TAE) monomer units. The TSA-POPs are fluorescent in the solid-state and responsive to Cu^{2+} and Pd^{2+}.

Excited-state intramolecular proton transfer (ESIPT)[1] is a phototautomerization that occurs when a chromophore containing an intramolecular proton donor (-OH, -NH_2) and proton acceptor (-C=O, -C=N-) are in close proximity. A key feature of ESIPT is a large Stokes shifted emission without self-absorption, which emanates from a rapid photoinduced enol-keto tautomerization process (Scheme 1). This unique feature makes chromophores that exhibit ESIPT potentially useful for the construction of laser dyes,[2] photostabilizers,[3] chemical sensors,[4] and optoelectronic devices.[5] Although the ESIPT properties of various single-molecule systems[6] and one-dimensional (1D)[7] polymers have been evaluated, two-dimensional (2D)[8] polymeric materials that exhibit ESIPT are extremely rare. Recently, we have demonstrated that tris(*N*-salicylideneaniline) (TSA) chromophores containing preformed C=N•••H-O bonds exhibit enhanced luminescent properties in the solid-state due to their ability to undergo efficient ESIPT to form the keto tautomer.[9] However, utilizing TSA chromophores to construct imine-linked 2D porous organic polymers (POPs)[10] that can undergo ESIPT has not been reported to date.

POPs are a unique class of amorphous porous polymers that have been utilized for applications related to gas storage,[11] separations,[12] catalysis,[13] and energy storage.[14] Although a number of POPs such as conjugated microporous polymers (CMPs),[15] polymers of intrinsic microporosity (PIMs),[16] porous aromatic frameworks (PAFs),[17] covalent triazine frameworks (CTFs),[18] covalent organic polymers (COPs)[19]and porous polymer frameworks (PPFs)[20] have been synthesized employing various fluorescent π-conjugated units, only a limited number exhibit luminescence. The absence of luminescence in these systems is mostly attributed to aggregation caused quenching (ACQ), which often occurs due to the strong π-π interactions between the adjacent layers of the material. However, a majority of the POPs that exhibit fluorescence in the solid-state is credited to an aggregation-induced emission (AIE) mechanism.[21] AIE typically relies on the restricted intramolecular rotation or motion of the π-conjugated units to produce a luminescence response. As a consequence, only a handful of π-conjugated monomers can be used to produce the desired AIE-based luminescence. Developing POPs that can undergo ESIPT could provide an alternative strategy for constructing luminescent materials without relying on the π-π interactions of carefully selected π-conjugated monomers. Such investigations could also be useful for designing other novel 2D polymeric systems for optoelectronic applications.



Scheme 1 Schematic representation of the ESIPT enol-keto tautomerization process for the TSA-Based POPs.

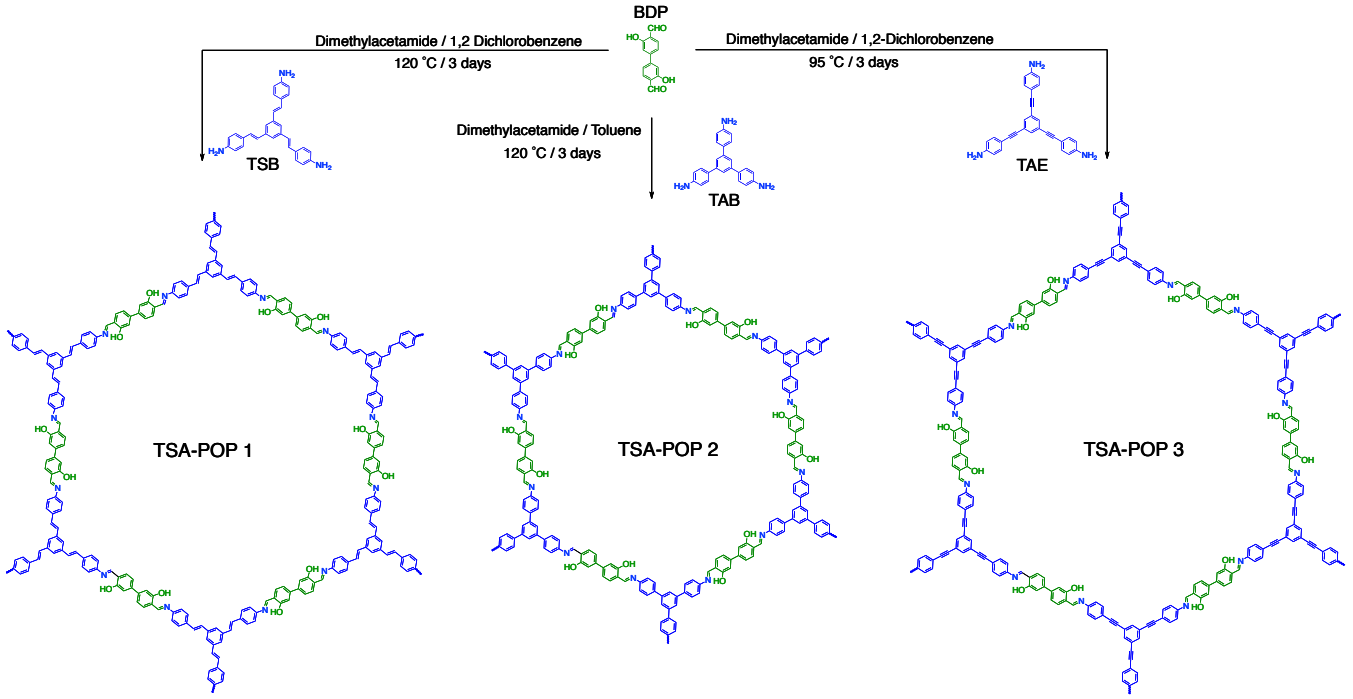
Herein, we report the synthesis of three imine-linked 2D TSA-POPs containing C_3-symmetric 1,3,5-triarylbenzene (TAB), -tristyrylbenzene (TSB), and -tris(arylethynyl)benzene (TAE) monomer units. We demonstrate that the preformed C=N•••H-O

Department of Chemistry & Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, Ohio 43210 (USA), Email: mcgrier.1@osu.edu.
Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7TC00123A

Journal Name

COMMUNICATION



Scheme 2 Synthesis of the TSA-POPs 1-3.

bonds of the TSA-POPs can undergo ESIPT to produce fluorescent materials with respectable surface areas. The TSA-POPs also experience quenching of fluorescence in the presence of Cu^{2+} and Pd^{2+} metal ions making them potentially useful for sensory applications. [22]

The imine-linked POPs were synthesized by reacting the amino functionalized TSB, TAB, and TAE monomers with 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (BDP) in a mixture of solvents containing 6M acetic acid at 95°C or 120 °C for three days to produce TSA-POPs 1-3, respectively (Scheme 2). The TSA-POPs were obtained by filtration and washed with tetrahydrofuran (THF) to obtain yellow powders that were insoluble in organic solvents. The optimal reaction conditions were obtained by screening different solvent mixtures, reaction times, and temperatures (Tables S1-S3, ESI). Thermogravimetric analysis (TGA) implied that the TSA-POPs are stable up to 400 °C (Fig S2-S4, ESI), while the scanning electron microscopy (SEM) images revealed a cauliflower-like morphology for the materials (Fig S5-S7, ESI).

The TSA-POPs were characterized using Fourier Transform infrared (FT-IR) and ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopies. The FT-IR spectra revealed the characteristic C=N stretching vibrations for the imine-linkage at ~1612 cm^{-1} (Fig. S8-S10, ESI). The ^{13}C CP-MAS spectra displayed the distinct resonance for the C=N bond at ~161 ppm for all of the TSA-POPs (Fig. S11-S13, ESI). The presence of the alkene and alkynyl units for TSA-POP 1 and 3 were confirmed at resonances of ~127.9 and 90.8 ppm, respectively. Powder x-ray diffraction (PXRD) profiles of the TSA-POPs revealed no peaks indicating that the materials are amorphous and exhibit no long-range order (Fig S14-S16, ESI).

The porosity of the TSA-POPs was evaluated using nitrogen gas adsorption isotherms at 77 K (Fig. 1). All three of the TSA-POPs exhibited reversible type IV isotherms, which is indicative of their mesoporosity. Applying the Brunauer-Emmett-Teller (BET) model over the low-pressure region ($0.04 < P/P_0 < 0.24$-0.29) provided surface areas of 601, 427, and 135 $m^2\ g^{-1}$ for TSA-POP 1, 2, and 3, respectively (Fig. S23-S25, ESI). The nonlocal density functional theory (NLDFT) pore size distributions revealed major peaks at 2.1,

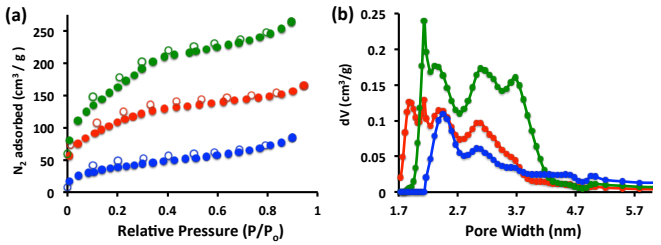


Fig. 1 Nitrogen adsorption-desorption isotherms (a) and NLDFT pore size distributions (b) for TSA-POP-1 (green), TSA-POP-2 (red), and TSA-POP-3 (blue) measured at 77 K.

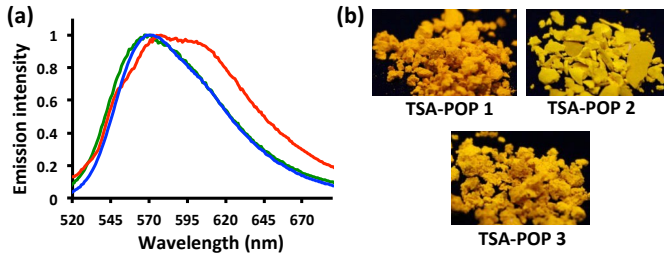


Fig. 2 Solid-State emission spectra (a) of TSA-POP 1 (red), TSA-POP 2 (green), and TSA-POP 3 (blue). (b) Photographs of the luminescent TSA-POPs taken using a hand-held UV-lamp at 365 nm.

2.1, and 2.5 nm for TSA-POP 1, 2, and 3, respectively, in addition to other pores that extend into the mesoporous range. The total pore volumes, which were calculated at single point values (P/P_0 = 0.94, 0.90, 0.89), provided values of 0.40, 0.20, and 0.12 $cm^3\ g^{-1}$ for TSA-POP 1, 2, and 3, respectively.

The solid-state emission spectra and luminescent photographs of TSA-POPs 1, 2, and 3 are shown in Fig. 2. TSA-POP 2 and 3 exhibit a λ_{max} of 565 nm and 567 nm, respectively. In comparison, the emission maxima of TSA-POP 1 displays a bathochromic shift of ~ 8-10 nm with a λ_{max} of 575 nm. The bathochromic shift could be attributed to the restricted rotation of the alkene units of the TSB linker, which leads to enhanced π-conjugation by reducing the energy gap of the π–π* transition for TSA-POP 1. This phenomenon is consistent with what has been observed for the previously reported alkene-based TSA analog.[9] Interestingly, the TAB and TAE linkers do not appear to have a significant effect on the bulk fluorescent properties of the materials. UV-Vis diffuse reflectance spectra show that the TSA-POPs exhibit broad absorption bands that extend from 380 nm to 550 nm (Fig. S17, ESI).

In an effort to verify that the materials are indeed undergoing ESIPT, we titrated suspensions of the TSA-POPs in THF with trifluoroacetic acid (TFA). Upon the addition of 0-75 μL TFA, the

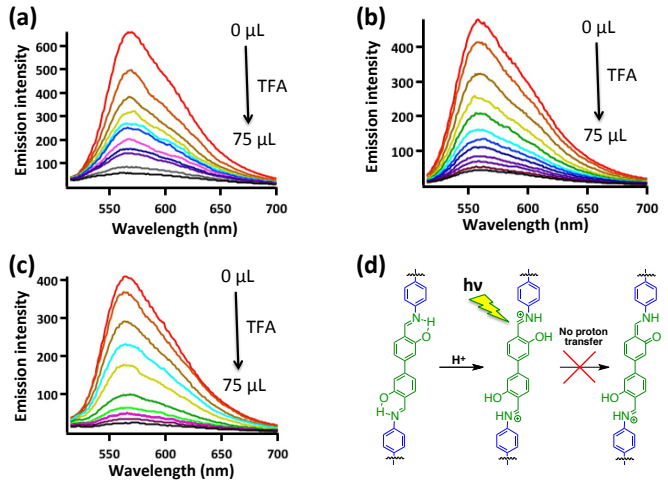


Fig. 3 Emission titration spectra of TSA-POP 1 (a), TSA-POP 2 (b), and TSA-POP 3 (c) with TFA suspended in THF. (d) Schematic representation of TFA inhibiting the ESIPT tautomerization process.

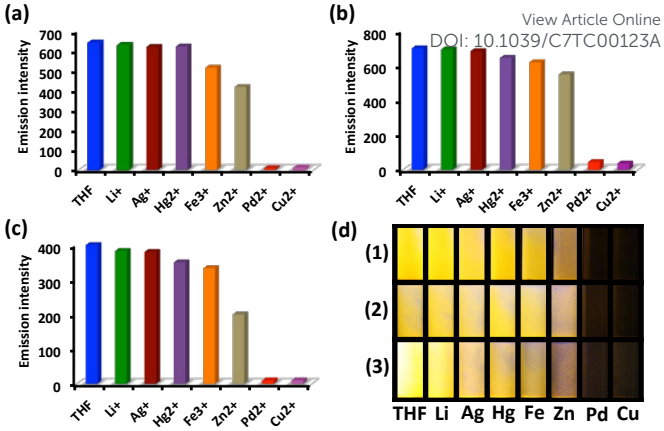


Fig. 4 Emission intensities of TSA-POP 1 (a), TSA-POP 2 (b), and TSA-POP 3 (c) suspended in THF before and after the addition of metal ions. (d) Photographs of TSA-POP 1 (1), TSA-POP 2 (2), and TSA-POP 3 (3) suspended in THF before and after the additon of metal ions. The pictures were taken taken using a hand-held UV-lamp at 365 nm.

emission bands of the TSA-POPs began to decrease in intensity, which eventually leads to the quenching of fluorescence (Fig 3a-3c). We believe the quenching of fluorescence is attributed to the suppression of the enol-keto tautomerization in the excited-state due to the protonation of the imine nitrogen atoms (Fig. 3d). In addition, it should be noted that the solid-state fluorescence of the TSA-POPs is highly dependent on the structure of the aldehyde precursor. For example, it has been shown that a 2,5-dihydroxyterephthalaldehyde (Dha) linker can be used to construct crystalline imine-linked covalent organic frameworks (COFs)[23], but to the best of our knowledge the materials do not undergo ESIPT in the solid-state. To verify this, we constructed the COF-DhaTab previously reported by Banerjee[23c] and compared it's photophysical properties to TSA-POP 2, which contains the extended BPD linker. Surprisingly, COF-DhaTab was not fluorescent in the solid-state, while TSA-POP 2 exhibited a bright yellow fluorescent color (Fig. S18, ESI). We believe the absence of fluorescence for COF-DhaTab could be attributed to 1) the ability of the stacked layers to undergo an ACQ mechanism, or 2) the weakened photoacidity of the Dha hydroxyl groups due to having both substituents attached to the same phenyl ring. The latter could inhibit the ability of the preformed C=N•••H-O bonds to undergo ESIPT in the solid-state.

In an effort to explore the ability of the TSA-POPs to function as fluorescent probes for metal ions on account of their preformed C=N•••H-O bonds, we evaluated the chemosensing ability of the materials in the presence of Li^+, Ag^+, Hg^{2+}, Fe^{3+}, Zn^{2+}, Pd^{2+}, and Cu^{2+} in THF (Fig. 4). TSA-POP 1, 2 and 3 all undergo quenching of fluorescence upon the excess addition of 180 μM Pd^{2+} and Cu^{2+} in tetrahydrofuran (THF) (Fig. S19-S21, ESI). Interestingly, the addition of Zn^{2+} results in a decrease in emission intensity for the TSA-POPs, which is different in contrast to the enhancement in fluorescence that was experienced for the TSA analogs.[9] The difference in fluorescent properties could be attributed to the inability of the rigid TSA-POPs to form 1:2 complexes with Zn^{2+}, which could impede an efficient metal-to-ligand charge transfer (MLCT) or

ligand-to-metal charge transfer (LMCT) process. Suspensions of the TSA-POPs were unresponsive to Li^{+}, Ag^{+}, Hg^{2+}, and Fe^{3+} in THF (Fig. S22, ESI).

In conclusion, we have demonstrated that a BDP linker and C_3-symmetric amino-functionalized monomers can be used to construct imine-linked TSA-POPs that can undergo ESIPT to produce luminescent materials. The TSA-POPs are also responsive to Cu^{2+} and Pd^{2+} making them potentially useful as fluorescent-based chemosensors.[24] To the best of our knowledge, this is the first example of 2D POPs exhibiting ESIPT in the solid-state. We believe such investigations are necessary for not only advancing the structural diversity of this unique class of materials, but also designing novel functional 2D polymers for practical applications.

Acknowledgements

P.L.M acknowledges the National Science Foundation (NSF) and Georgia Tech Facilitating Academic Careers in Engineering and Science (GT-FACES) for a Career Initiation Grant, and funding from The Ohio State University. We thank Katja Meyer and Dr. Umit Ozkan for assistance with the TGA measurements.

Notes and references

[1] (a) C.-C. Hsieh, C.-M. Jiang, P.-T. Chou, *Acc. Chem. Res.* **2010**, *43*, 1364-1374; (b) J. E. Kwon, S. Y. Park, *Adv. Mater.* **2011**, *23*, 3615–3642; (c) V. I. Tomin, A. P. Demchenko, P.-T. Chou, *J. Photochem. Photobiol., C* **2015**, *22*, 1-18. (d) V. S. Padalkar, S. Seki, *Chem. Soc. Rev.* **2016**, *45*, 169-202.

[2] (a) A. U. Khan, M. Kasha, *Proc. Natl. Acad. Sci. USA* **1983**, *80*, 1767 –1770. (b) K.-i. Sakai, M. Ichikawa, Y. Taniguchi, *Chem. Phys. Lett.* **2006**, *420*, 405-409.

[3] (a) M. J. Paterson, M. A. Robb, L. Blancafort, A. D. DeBellis, *J. Phys. Chem. A* **2005**, *109*, 7527–7537; (b) Y. Gong, Z. Wang, S. Zhang, Z. Luo, F. Gao, H. Li, *Ind. Eng. Chem. Res.* **2016**, *55*, 5223–5230.

[4] (a) Q. Chu, D. A. Medvetz, Y. Pang, *Chem. Mater.* **2007**, *19*, 6421–6429; (b) B. Liu, H. Wang, T. Wang, Y. Bao, F. Du, J. Tian, Q. Li, R. Bai, *Chem. Commun.* **2012**, *48*, 2867-2869; (c) J. Zhao, S. Ji, Y. Chen, H. Guo, P. Yang, *Phys. Chem. Chem. Phys.* **2012**, *14*, 8803-8817.

[5] S.-J. Lim, J. Seo, S. Y. Park, *J. Am. Chem. Soc* **2006**, *128*, 14542-14547.

[6] (a) T. Arthen-Engeland, T. Bultmann, N. P. Ernsting, M. A. Rodriguez, W. Thiel *Chem. Phys.* **1992**, *163*, 43-53; (b) D. W. Brousmiche, P. Wan, *J. Photochem. Photobiol. A: Chem.* **2000**, *130*, 113-118; (c) N. Otsubo, C. Okabe, H. Mori, K. Sakota, K. Amimoto, T. Kawato, H. Sekiya, *J. Photochem. Photo- biol. A* **2002**, *154*, 33−39 ; (d) M.-W. Chung, T.-Y. Lin, C.-C. Hsieh, K.-C. Tang, H. Fu, P.-T. Chou, S.-H. Yang, Y. Chi, *J. Phys. Chem. A* **2010**, *114*, 7886–7891; (e) T. Sekikawa, O. Schalk, G. Wu, A. E. Boguslavskiy, A. Stolow, *J. Phys. Chem. A* **2013**, *117*, 2971−2979; (f) Benelhadj, W. Muzuzu, J. Massue, P. Retailleau, A. Charaf-Eddin, A. D. Laurent, D. Jacquemin, G. Ulrich, R. Ziessel, *Chem. Eur. J* **2014**, *20*, 12843-12857; (g) K. Skonieczny, J. Yoo, J. M. Larsen, E. M. Espinoza, M. Barbasiewicz, V. I. Vullev, C.-H. Lee, D. T. Gryko, *Chem. Eur. J* **2016**, *22*, 7485 –7496; (h) P. Singh, H. Singh, R. Sharma, G. Bhargava, S. Kumar, *J. Mater. Chem. C* **2016**, *4*, 11180-11189.

[7] (a) R. M. Tarkka, X. Zhang, S. A. Jenekhe, *J. Am. Chem. Soc.* **1996**, *118*, 9438-9439; (b) D. W. Chang, S. Kim, S. Y. Park, *Macromolecules* **2000**, *33*, 7223-7225; (c) S. Park, S. Kim, J. Seo, S. Y. Park, *Macromolecules* **2005**, *38*, 4557-4559; (d) K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevičius, S. Tamulevičius, V. Gulbinas, S. Ando, *Macromolecules* **2016**, *49*, 1848-1857.

[8] J. W. Colson, W. R. Dichtel, *Nat. Chem.* **2013**, *5*, 453–465.

[9] P. Jagadesan, T. Whittemore, T. Beirl, C. Turro, P. L. McGrier, Chem. Eur. J **2016**, DOI: 10.1002/chem.201604315.

[10] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.* **2012**, *112*, 3959-4015.

[11] (a) R. Dawson, E. Stockel, J. R. Holst, D. J. Adams, A. I. Cooper, *Energy Environ. Sci.* **2011**, *4*, 4239-4245; (b) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat Commun.* **2013**, *4*, 1960–1965. (c) H. A. Patel, D. Ko, C. T. Yavuz, *Chem. Mater.* **2014**, *26*, 6729−6733; (d) S. Bandyopadhyay, A. G. Anil, A. James, A. Patra, *ACS Appl. Mater. Interfaces* **2016**, *8*, 27669−27678.

[12] (a) C. D. Wood, B. Tan, A. Trewin, H. Niu, D. Bradshaw, M. J. Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stockel, A. I. Cooper, *Chem. Mater.* **2007**, *19*, 2034–2048; (b) C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou, A. I. Cooper, *Adv. Mater.* **2008**, *20*, 1916–1921; (c) S. Yuan, B. Dorney, D. White, S. Kirklin, P. Zapol, L. Yu, D.-J. Liu, *Chem. Commun.* **2010**, *46*, 4547–4549.

[13] P. Kaur, J. T. Hupp, S. T. Nguyen, *ACS Catal.* **2011**, *1*, 819–835.

[14] (a) J.-X. Jiang, A. Trewin, D. J. Adams, A. I. Cooper, *Chem. Sci.* **2011**, *2*, 1777-1781; (b) A. Thomas, P. Kuhn, J. Weber, M.-M. Titirici, M. Antonietti, *Macromol. Rapid Commun.* **2009**, *30*, 221–236.

[15] (a) J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem. Int. Ed.* **2007**, *46*, 8574 –8578; (b) L. Chen, Y. Honsho, S. Seki, D. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 6742−6748; (c) G. Cheng, T. Hasell, A. Trewin, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* **2012**, *51*, 12727-12731; (d) B. Bonillo, R. S. Sprick, A. I. Cooper, *Chem. Mater.* **2016**, *28*, 3469−3480.

[16] N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675–683.

[17] T. Ben, S. Qiu, *CrystEngComm* **2013**, *15*, 17-26.

[18] C. E. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas, L. Prati, *Nano Lett.* **2010**, *10*, 537–541.

[19] Z. Xiang, D. Cao, L. Dai, *Polym. Chem.* **2015**, *6*, 1896-1911.

[20] Y. Zhu, H. Long, W. Zhang, *Chem. Mater.* **2013**, *25*, 1630–1635.

[21] S. Dalapati, C. Gu, D. Jiang, *Small* **2016,** *12*, 6513-6527.

[22] (a) W.-L. Gong, M. P. Aldred, G.-F. Zhang, C. Li, M.-Q. Zhu, *J. Mater. Chem. C*, **2013**, *1*, 7519-7525; (b) L. Guo, D. Cao, *J. Mater. Chem. C* **2015**, *3*, 8490-8494; (c) D. Ma, B. Li, Z. Cui, K. Liu, C. Chen, G. Li, J. Hua, B. Ma, Z. Shi, S. Feng, *Appl. Mater. Int.* **2016,** *8*, 24097-24103.

[23] (a) S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine, R. Banerjee, *Angew. Chem. Int. Ed.* **2013**, *52*, 13052 - 13056; (b) X. Chen, M. Addicoat, E. Jin, L. Zhai, H. Xu, N. Huang, Z. Guo, L. Liu, S. Irle, D. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 3241-3247; (c) S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma, R. Banerjee, Nat. Commun. 2015, 6, 6786-6795.

[24] L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, *Coord. Chem. Rev.* **2000**, *205*, 59-83.

View Article Online
DOI: 10.1039/C7TC00123A

View Article Online
DOI: 10.1039/C7TC00123A

The excited-state intramolecular proton transfer (ESIPT) properties of three tris(*N*-salicylideneaniline)-based (TSA) imine-linked porous organic polymers (POPs) were investigated.