CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Exploration of Thiazolo[5,4-d]thiazole Linkages in Conjugated Porous Organic Polymers for Chemoselective Molecular Sieving

Authors: Bishnu Prasad Biswal, Daniel Becker, Naisa Chandrasekhar, Jensheer Shamsudeen Seenath, Silvia Paasch, Susanne Machill, Felix Hennersdorf, Eike Brunner, Jan J. Weigand, Reinhard Berger, and Xinliang Feng

To be cited as: *Chem. Eur. J.* 10.1002/chem.201802631

Link to VoR: http://dx.doi.org/10.1002/chem.201802631

Supported by
ACES

WILEY-VCH

Exploration of Thiazolo[5,4-*d*]thiazole Linkages in Conjugated Porous Organic Polymers for Chemoselective Molecular Sieving**

Bishnu P. Biswal,[a],‡ Daniel Becker,[a],‡ Naisa Chandrasekhar,[a] Jensheer Shamsudeen Seenath,[a] Silvia Paasch,[b] Susanne Machill,[b] Felix Hennersdorf,[c] Eike Brunner,[b] Jan J. Weigand,[c] Reinhard Berger,*[a] Xinliang Feng*[a]

Abstract: Porous Organic Polymers (POPs) have attracted significant attention towards molecular adsorption in recent years due to their high porosity, diverse functionality and excellent chemical stability. In this work, we present a systematic case study on the formation of thiazolo[5,4-*d*]thiazole (TzTz) linkages through model compounds and its integration to synthesize a set of three novel, thermo-chemically stable TzTz-linked POPs, namely **TzTz-POP-3**, **TzTz-POP-4**, and **TzTz-POP-5** with triphenylbenzene, tetraphenylpyrene and tetra(hydroxyphenyl)methane cores respectively. Interestingly, the integrated TzTz moiety of the represented **TzTz-POP-3** renders chemoselective removal of organic dye Fluorescein (FL) from a mixture with Parafuchsin (FU) in aqueous solution. The **TzTz-POP-3** offered excellent chemoselectivity of ~1: 7 (FL: FU), compared to alike porous materials demonstrated for similar applications due to the presence of multiple active anchoring sites coupled with permanent porosity and appropriate pore window.

Introduction

Synthesis of conjugated porous organic networks[1-3] through covalent linkages is of particular interest in current materials research owing to their wide range of applications in the area of molecular adsorption,[4] optoelectronics,[5] catalysis,[6] separation,[7-9] sensing,[10] and energy conversion/storage.[11] In this context, porous organic polymers (POPs)[12-18] and covalent organic frameworks (COFs)[19-24] are the two front line members distinguished by structural orderings. In general, COFs are crystalline while POPs are amorphous in nature, although both have adequate porosity.[25] Typically, POPs are formed by using irreversible organic reactions such as Suzuki cross-coupling reaction, Yamamoto reaction, cyclotrimerization, etc. Thus, the resulting framework possess exceptional chemical stability due to the formation of strong covalent aryl-aryl bonds.[6,26-28] Since POPs feature high chemical stability, functional groups and scalable protocols starting from a broad range of monomers, they are preferred for many applications.[1,2,25] Despite the prompt advancement in the field, only few limited reactions have been employed so far, which could introduce heterocyclic units in the porous networks. Especially, introduction of fused heterocyclic units *e.g.* thiazolo[5,4-*d*]thiazole (TzTz) into a porous polymeric network is highly challenging as it involves expensive transition-metal-based catalysts and extra purification efforts, which restrict the up-scalable synthesis, although several linear TzTz-linked polymers are known.[29-31] In 2015, an one-pot and catalyst-free protocol for the synthesis of two TzTz-linked porous polymers was demonstrated and used for the selective CO_2 adsorption over N_2. Besides, this class of porous materials so far remain less explored due to the poor understanding of their formation and reaction pathways. Markedly, the integrated heterocyclic networks would be interesting for many applications especially adsorption of heavy metals, toxic gasses and organic molecules due to the availability of multiple anchoring sites in close proximity coupled with porosity.[32,33]

In this work, at first to understand the formation of TzTz linkage pathway, we performed a series of reactions of model compound with varying substituents and investigated their structural outcome by means of nuclear magnetic resonance (NMR) spectroscopy and X-ray single crystal analysis. As a result of substituent tailoring effect, we isolated a stable intermediate (E)-2-(5-((2-hydroxybenzylidene)amino)-4-mercaptothiazol-2-yl)phenol-dimer (abbreviated as **TzTz-M3-I**) in the reaction towards 2,5-di(2-hydroxyphenyl)thiazolo[5,4-d]thiazole (abbreviated as **TzTz-M3**). The structure of the intermediate (**TzTz-M3-I**) revealed an alternative pathway to the one that is currently discussed in literature,[33-36] which could be interesting and useful for the de novo design of TzTz-linked compounds and materials.

Subsequently, a set of three novel thiazolo[5,4-d]thiazole (TzTz)-linked POPs namely, **TzTz-POP-3**, **TzTz-POP-4**, and **TzTz-POP-5**, have been synthesized with a set of building units such as triphenylbenzene, tetraphenylpyrene and tetra(hydroxyphenyl)methane respectively. Due to the presence of elongated and functionalized building units in the resulting conjugated TzTz-POPs, they exhibit high porosities and thermo-chemical stabilities compared to the previously reported porous polymers with TzTz linkages.[33] By taking advantages of multiple anchoring sites in close proximity coupled with porosity of TzTz-POPs, we have utilized the integrated network for the chemoselective removal of Fluorescein (FL) dye in a mixture with Parafuchsin (FU) in aqueous solution. We have chosen **TzTz-POP-3** as a model system for the detailed dye adsorption study

---

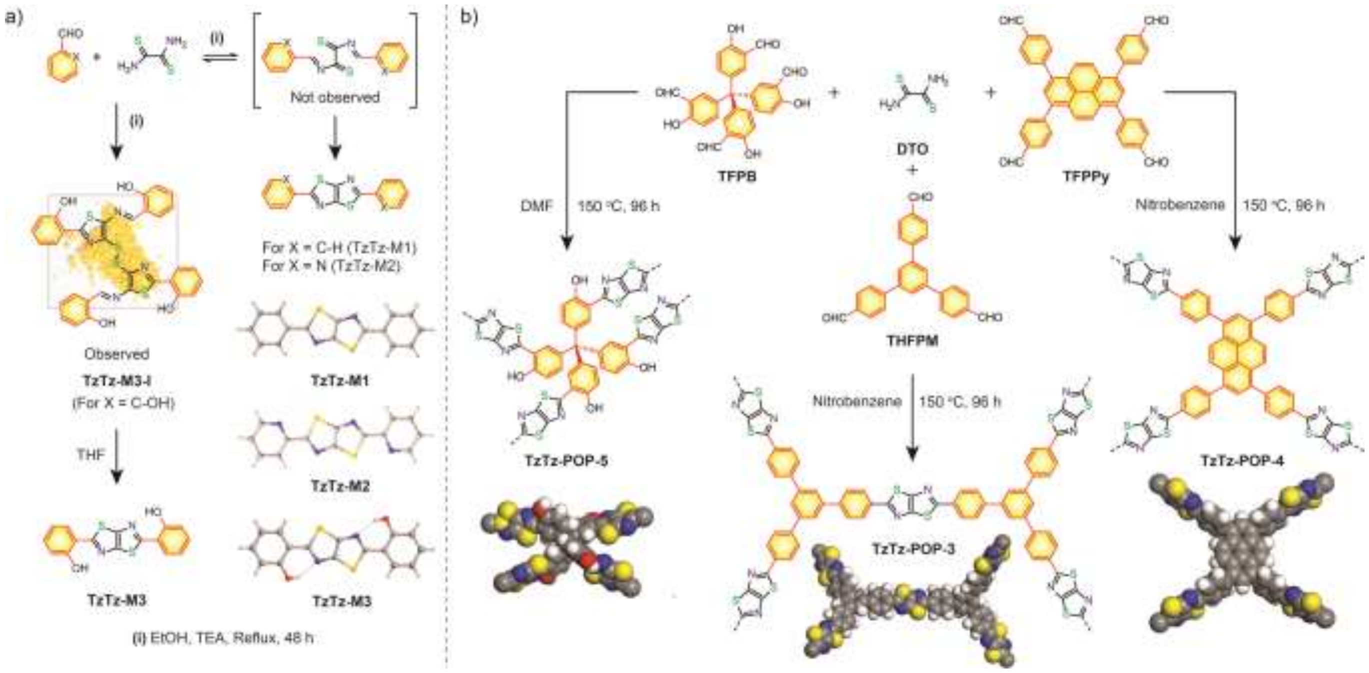
[a] Dr. B. P. Biswal, D. Becker, Dr. N. Chandrasekhar, J. S. Seenath, Dr. R. Berger and Prof. Dr. X. Feng
Faculty of Chemistry and Food Chemistry, Center for Advancing Electronics Dresden, Technische Universitat Dresden, 01062, Dresden, Germany.
E-mail: xinliang.feng@tu-dresden.de; reinhard.berger@tu-dresden.de

[b] Dr. S. Paasch, Dr. S. Machill and Prof. Dr. E. Brunner
Chair of Bioanalytical Chemistry, Technische Universität Dresden, 01062, Dresden, Germany.

[c] Dr. F. Hennersdorf and Prof. Dr. J. J. Weigand
Chair of Inorganic Molecular Chemistry, Technische Universität Dresden, 01062 Dresden, Germany.

[‡] These authors contributed equally to this work.

Supporting Information and the ORCID number(s) for the author(s) of this article can be found under https://doi.org/xxxxxxxxxxxxxx.



Scheme 1. a) Schematic illustration of the synthesis of model compounds based on thiazolo[5,4-d]thiazoles (TzTz) linkage and intermediate; b) Synthesis route of TzTz linked Porous Organic Polymers (POPs) from different symmetrical arylaldehydes and dithiooxamide (DTO, spacefilling model of optimized fragments of **TzTz-POP-3, -4** and **-5** created using Materials Studio version 2017, presented at the bottom to represent the local structure of TzTz-POPs).

as it possesses appropriate pore size (~13 Å, suitable for both the dyes) and without any additional functional groups. Notably, **TzTz-POP-3** exhibits excellent selectivity of ~1:7 compared to alike porous materials demonstrated for similar applications. The selective adsorption can be attributed to the preferred intermolecular H-bonding interactions of the —OH groups of FL compared to the —NH_2 groups presented in FU dye with the TzTz moieties.

Result and Discussion

Structural analysis of model compounds

At the beginning, we expected to achieve the simple Schiff base condensation products[36] of *ortho*-substituted arylaldehydes and DTO (Figure 1a), which could be further cyclised into the stable TzTz moiety. Assuming that, our strategy would lead to the formation of crystalline polymers due to the dynamic nature of Schiff base when extended with symmetrical linkers. Keeping this in mind, we have synthesized two model compounds in refluxing ethanol and triethylamine (TEA) by reacting DTO with benzaldehyde to obtain 2,5-diphenylthiazolo[5,4-*d*]thiazole (**TzTz-M1**),[37] and 2-pyridinecarboxaldehyde to obtain 2,5-di(pyridin-2-yl)thiazolo[5,4-*d*]thiazole (**TzTz-M2**),[38] respectively (see Scheme 1a). In both cases, only doubly cyclised TzTz products of **TzTz-M1** and **TzTz-M2** were isolated and characterised in full. However, when attempted the synthesis of 2,5-di(2-hydroxyphenyl)thiazolo[5,4-*d*]thiazole[39] (**TzTz-M3**) under the same conditions, we found that the collected precipitate (63% yield) was neither the expected final doubly cyclised TzTz product nor the two-sided Schiff base product as a result of coupling between the DTO and salicyladehyde. Using two-dimensional heteronuclear single quantum coherence (2D-HSQC) NMR spectroscopy and high-resolution electrospray ionisation mass spectrometry (HR-ESI$^+$ MS) (Figure 1a and 1b; Section S3, Figure S3 and S5 in the Supporting Information) studies, we identified, the dimeric, partially cyclised (thiazole) intermediate **TzTz-M3-I** (Scheme 1a and Figure 1a). From 2D-NMR, it has been confirmed that the two identical molecular parts are bridged *via* S-S linkages. HR-ESI$^+$ mass also give a clear signal of *m/z* 655.059, which supports the proposed dimeric structure of the intermediate. Moreover, the existence of S-S linkage can be validated using Fourier Transform Infrared and Raman spectroscopy (Figure 1c and 1d; Figure S7 in the Supporting Information). In the FT-IR spectra of intermediate, **TzTz-M3-I** a band at 447 cm^{-1} and two bands 650 and 692 cm^{-1} corresponds well with S-S and C-S bonds. The Raman spectrum displace the S-S stretching vibration band centred at 446 cm^{-1} which is not observed in the case of final **TzTz** product i.e. **TzTz-M3**. The intermediate **TzTz-M3-I** was stable in the solid state for several months but it can be transformed into the fully cyclised product (**TzTz-M3**; 26% yield) under sonication for five minutes in solution (THF). Thus, we consider that the formation pathway of TzTz in solution goes through sequential formation of one side thiazole ring (Scheme 1a and Figure S10 in the Supporting Information). During the process, the intermediate (E)-2-(5-((2-hydroxybenzylidene)amino)-4-mercaptothiazol-2-yl)phenol is stabilized, which could be possible due to the intramolecular H-bonding between additional hydroxyl group and the nitrogen atom in the imine bond (C=N), resulting into the dimeric structure after oxidative disulfide bond formation. We propose a plausible pathway for the TzTz formation as given in Figure S10 in the Supporting Information. Thus, according to the outcome of model compounds synthesis, a fast and irreversible **TzTz** formation for **TzTz-M1** and **-M2**; and a stepwise formation for **TzTz-M3** can be concluded.

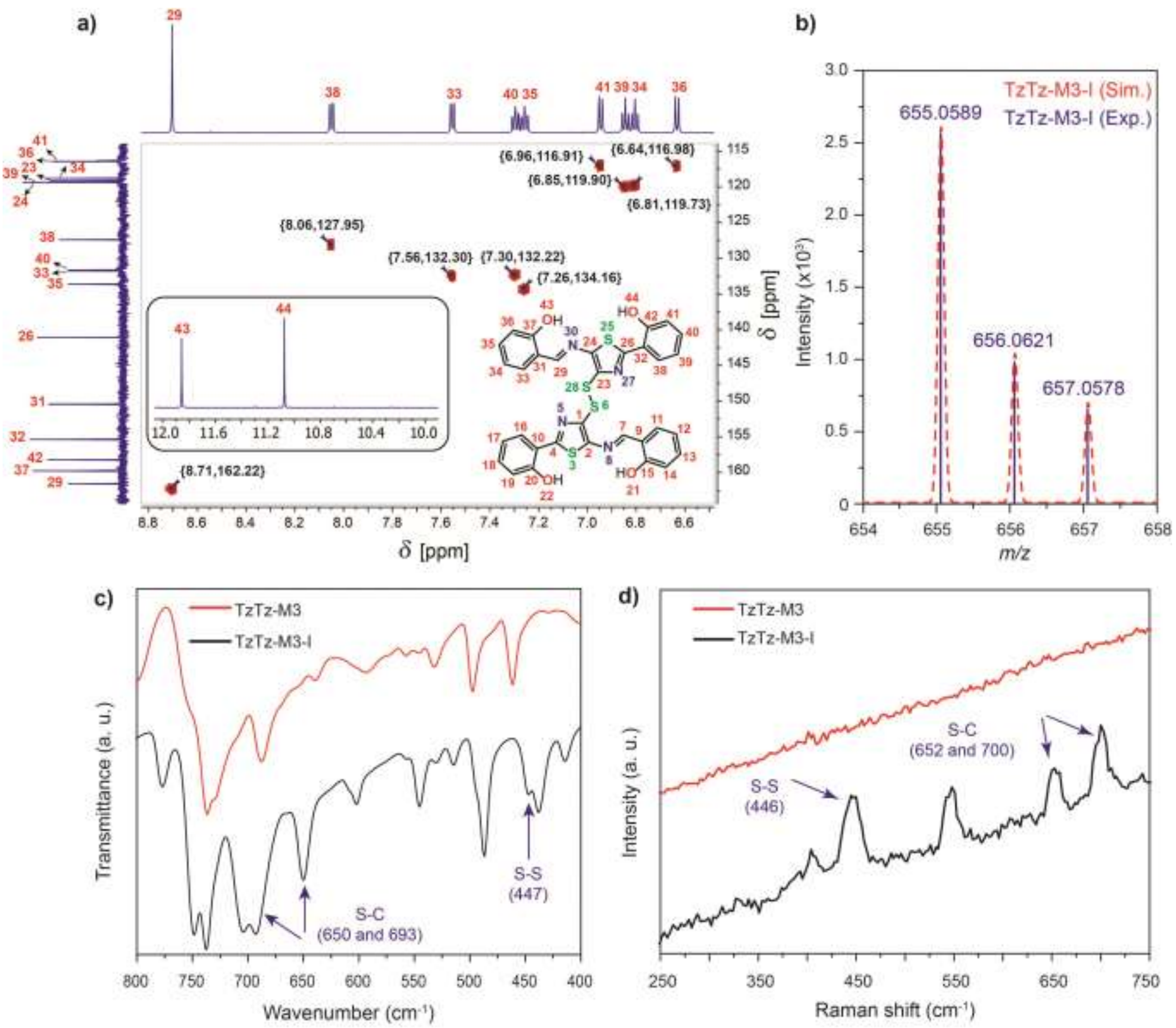


Figure 1. a) 2D (HSQC) NMR spectra measured in $(CD_3)_2SO$; b) High resolution ESI$^+$ mass spectrometry; c) FT-IR and d) Raman spectrum of the intermediate compound (**TzTz-M3-I**).

Synthesis and characterization of TzTz-POPs

Afterwards, three new porous polymers namely, **TzTz-POP-3**, **TzTz-POP-4**, and **TzTz-POP-5** using DTO and symmetrical arylaldehydes such as 1,3,5-tris(4-formylphenyl)benzene, 1,3,6,8-tetra(4-formylphenyl)pyrene, and tetra(4-fromyl-3-hydroxyphenyl)methane respectively under the catalyst-free solvothermal process have been prepared. All these POPs were isolated in very good yields (~80%) and are insoluble in almost all common organic solvents. All three POPs were obtained as amorphous solids according to our powder X-ray diffraction investigations (Figure S11 in the Supporting Information). To get a better insight into the functional groups, bond formation and the local mode of binding in the POPs, we have collected the FT-IR spectra from which we can identify the newly formed C=N bonds (ranging from 1580-1620 cm^{-1}). The absence of the C=O stretching vibration of the carbonyl group that are expected in the range of 1650-1692 cm^{-1}, indicates an efficient condensation to form the **TzTz** linkages. All three POPs [**TzTz-POP-3**, **-4**, and **-5**] displayed similar FT-IR spectra with only a little variation in the peak position with regards to the —C=N and —C-S bonds of the **TzTz** ring (Figure 12 in the Supporting Information). The structure of **TzTz-POP**s was determined by ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy (Figure 2a). The experimental spectra agree well with predicted ^{13}C NMR data calculated with the program ACD/Labs (Figure S13 in the Supporting Information).[40] All signals can be assigned to the respective carbon atoms. The spectra of all three compounds show the presence of aromatic groups (chemical shift region of ca. 120-150 ppm) as well as at higher chemical shifts of carbons of the heterocyclic **TzTz** ring corresponding to the building units. For **TzTz-POP-3** and **-4** these signals appear at δ = ~152 and ~168 ppm, whereas **TzTz-POP-5** shows the same signals at δ = 155.5 and 170.4 ppm respectively, due to the influence of hydroxyl groups. Compared to **TzTz-POP-3** and **-4** for **TzTz-POP-5** an additional signal for an aliphatic carbon is expected caused by the tetrahedral centre. This signal is clearly detected at δ = 62.8 ppm (see Figure 2a). In summary, the ^{13}C CP NMR spectra can visualize the structural differences of investigated **TzTz-POP**s and confirm the expected structures of these new compounds.

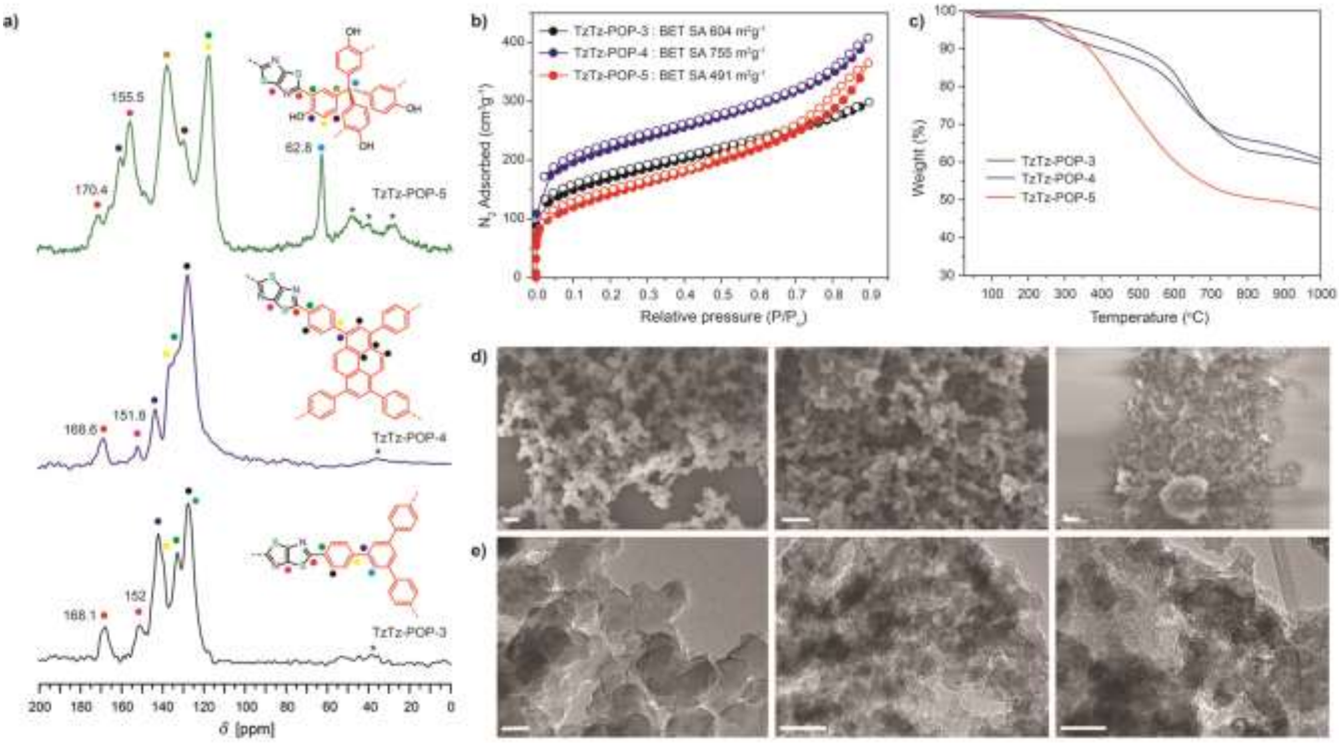


Figure 2. a) ^{13}C cross-polarization magic-angle spinning (CP-MAS) solid state NMR spectra, *denotes spinning sidebands; b) N_2 adsorption isotherms; c) Thermogravimetric analysis (TGA) profile; d) Scanning electron microscopy (SEM) images (Scale bar: 200 nm) and e) Transmission electron microscopy (TEM) images (Scale bar: 50 nm) of **TzTz-POP-3**, **-4**, and **-5** respectively.

In order to evaluate the thermal stability of all POPs [**TzTz-POP-3**, **-4** and **-5**], we have performed thermogravimetric analysis (TGA) under N_2. From the TGA profiles, it can be derived that all POP's pores are guest free and have almost identical thermal stability up to ~450 ºC (Figure 2c). However, **TzTz-POP-5** has a lower thermal stability and degradation starting from 300 ºC. After decomposition temperature, a gradual weight loss of ~40-50% for **TzTz-POP-3** and **TzTz-POP-4** and ~53% for **TzTz-POP-5**, were observed until a temperature of 1000 °C. From the TGA profiles, also it can be seen that all TzTz-POPs loss a weight of ~2% at 100 ºC, which could be attributed to moisture. However, for **TzTz-POP-4**, an additional weight loss of ~7% around 200 ºC, and this could corresponds to the trapped high boiling solvent (DMF) and oligomeric fragments.

External morphologies and permanent porosity

The external morphologies of the TzTz-POP materials were inspected by scanning electron microscopy (SEM). From the SEM images it is inferred that small semi-spherical particles (~100 nm) agglomerates to construct a colony for **TzTz-POP-3**. However, for **TzTz-POP-4** and **-5** the particles are even smaller and of size less than 50 nm (Figure 2d and Figure S17 in the Supporting Information). The similar trend and morphology has been also observed in transmission electron microscopy (TEM) images (Figure 2e and Figure S18 in the Supporting Information). Here, we would like to note that predicting the particle size and shape of any organic porous materials synthesized via solvothermal method is difficult and hard to explain. However, we assume that due to relatively less pi-pi stacking in the case of **TzTz-POP-4** and **-5** compared to **TzTz-POP-3** is the reason for the formation of smaller size particles even below 50 nm.

Nitrogen adsorption-desorption experiments were performed to examine the architectural rigidity, permanent porosity of all three POPs at 77 K (Figure 2b). The POPs were solvent (methanol/dichloromethane) exchanged and activated prior to analysis to make the pores guest free at 170 ºC for 16 h under vacuum. The fully reversible type-II isotherms show rapid uptake at low relative pressures indicating that all these polymers are mainly microporous in nature. The increase in the nitrogen adsorption at a high relative pressure (~0.8) may arise due to interparticulate porosity of the samples and voids. The Brunauer-Emmett-Teller (BET) surface areas of these POPs were found to be 604 m^2g^{-1} (**TzTz-POP-3**), 755 m^2g^{-1} (**TzTz-POP-4**) and 491 m^2g^{-1} (**TzTz-POP-5**) [Calculated over a relative pressure (P/P_0) range from 0.05 to 0.2] (Figure S14 and S15 in the Supporting Information). Notably, the surface area values of the **TzTz-POP**s are higher than the previously reported 299 m^2g^{-1} and 488 m^2g^{-1} for **TzTz-POP-1** and **-2** employing phenyl and tetraphenylmethane building units, respectively.[33] In addition, the pore size distribution (PSD) analysis has been derived from the N_2 isotherm data for all **TzTz-POP**s using nonlocal density functional theory (NLDFT), which suggests primary narrow micropores of the polymeric frameworks (Figure S14 in the Supporting Information).

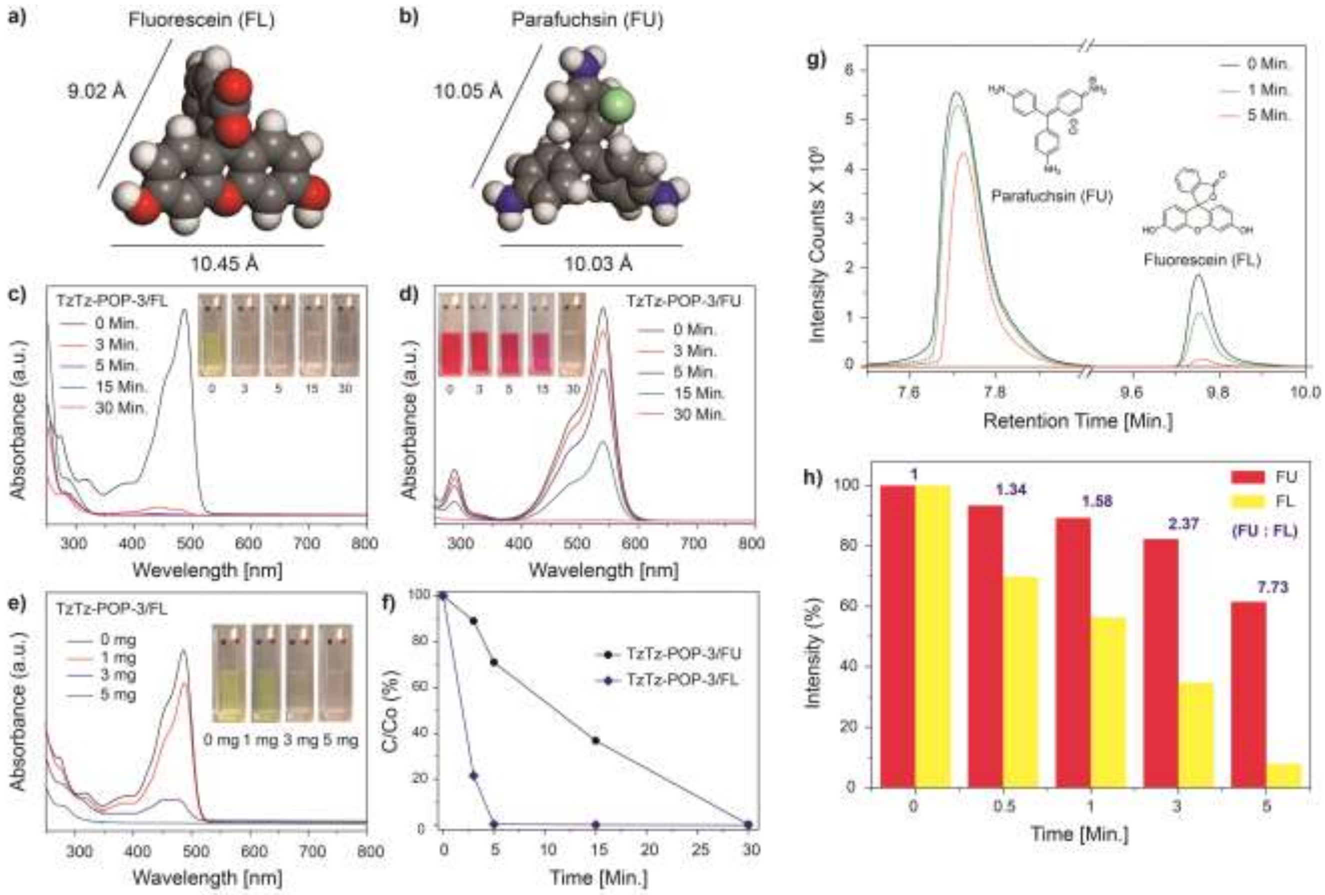


Figure 3. a) and b) spacefilling models of FL and FU generated using Materials studio version 2016; c) and d) Comparison of UV-vis absorption spectra of aqueous solutions of FL and FU after treatment with **TzTz-POP-3** at different intervals (Inset: real photographs of FL and FU before and after treatment with **TzTz-POP-3** at different intervals); e) UV-vis absorption spectra of aqueous solutions of FL before and after treatment with different amount of **TzTz-POP-3** for 5 mins. (Inset: real photographs of FL before and after treatment with **TzTz-POP-3** at different doses); f) Change in concentration of dyes (FL and FU) over time after treatment with **TzTz-POP-3**, determined by change in absorbance relative to initial absorbance (C/C0); g) Sections of chromatogram measured by HPLC-MS of 1:1 (molar ratio) mixture of FU and FL, before and after treatment with **TzTz-POP-3** [Solid line: blank (1:1 mixture); green dotted line: after 1 min.; red dotted line: after 5 mins.; with peaks 7.7 and 9.75 mins. retention times for FU and FL respectively (extracted ion plots of the protonated molecules are presented); h) Change in concentration of dyes (FU and FL) over time after treatment with **TzTz-POP-3**, determined from the peak areas of HPLC measurements (1:1 mixture of FU and FL is considered as 100%). The ratio of FU to FL intensity counts (in %) is presented as blue font text.

Optical properties

Further, to understand the optoelectronic properties of the synthesized POPs, we performed UV-vis absorption in integrating sphere in the dispersion state and photoluminescence measurements. **TzTz-POP-3**, **-4** and **-5** showed broad optical absorption centred at wavelengths around 400 nm, 422 nm and 414 nm respectively. These are in agreement with a similar absorption maximum observed for the model compound (see Figure S8 in the Supporting Information) with a maximum absorption at 382 nm and 402 nm. For all three TzTz-POPs a tailing absorption and emission can be found above 550 nm, which is attributed to the increased conjugation of TzTz linkages (Figure S16 in the Supporting Information).

Chemoselective dye adsorption

Taking the advantages of high porosity, excellent chemical stability and multiple anchoring sites of fused heterocyclic moiety of **TzTz-POP**s, we were motivated to investigate the dye adsorption[41] of practical significance from aqueous solution. For our purpose, we have intentionally selected two different organic dyes, namely, FU and FL containing —NH_2 and —OH groups respectively and studied the effect of functionality towards adsorption.[42] As depicted in Figure 3, the molecular dimension of FU (10.03 Å x 10.05 Å) and FL (10.45 Å x 9.02 Å) was calculated based on the optimized structure using Material Studio 2016. Both the dye molecules have almost same dimensional size but different functionality as mentioned above and suitable for the selective adsorption study. We have used UV-vis spectroscopy to monitor the change of concentration of the individual dyes at a fixed time interval upon treatment with **TzTz-POP-3**. We have chosen **TzTz-POP-3** for the detailed dye adsorption study as it possesses good porosity with suitable pore size (~13 Å, based on PSD, Figure S14 in the Supporting Information) and does not contain any additional functional groups except the **TzTz** linkage. To our delight, **TzTz-POP-3** has the capability to quickly adsorb and remove organic dye (FL) from water as compared to FU (Figure 3c and 3d). As shown in Figure 3c and 3d, the dye FL was almost removed within 5 min., showing a removal efficiency of ~99.6%, while the FU, which contains —NH_2 groups, exhibited only ~29% removal efficiency at the same time confirmed from UV-vis spectroscopy.

In addition, we checked the effect of dose of adsorbent on dye adsorption by performing individual batch experiments with

1 mg, 3 mg and 5 mg of **TzTz-POP-3** in 5 ml of FL stock solution in water (Figure 3e). From absorption measurement, we found that 5 mg of **TzTz-POP-3** was sufficiently enough to adsorb FL completely (~99.5%) within 5 min. from aqueous solution. We consider that, the basic **TzTz** moiety of the **TzTz-POP-3** helps to discriminate functional groups and selectively interact with –OH, over $-NH_2$ groups under neutral condition. Similar phenomenon has been recently reported by Ning et al. wherein basic —N-H functionality selectively interacts with the —OH groups over —NH_2 to facilitate chemoselective separation in salicylideneanilines-based COFs.[43] We further investigated the chemoselective ability of **TzTz-POP-3** in the mixture as it has higher and faster uptake capacity towards —OH containing (FL) dye over —NH_2 based (FU) Dye. Towards this end, **TzTz-POP-3** powder was suspended in aqueous solution of both FL and FU (~50 µmol each; 1: 1 ratio by Vol.) and collected the samples at different time intervals such as 30 sec, 1 min., 3 min., 5 min., and 15 min., respectively. We performed HPLC and noticed that the concentration of FL was largely decreased to ~8% (considered FL peak from the 1: 1 mixture of FL: FU as 100%), whereas FU decreased to 62% within 5 min., resulting into an excellent selectivity with a ratio of 1: 7.7 for FL: FU in the filtrate (Figure 3g, 3h and Figure S20 in the Supporting Information).

Finally, to showcase the reusability of **TzTz-POP-3** towards dye adsorption, we have washed the colored **TzTz-POP-3** using *N*,*N*-dimethylacetamide (DMAc) under stirring overnight, followed with ethanol and acetone. The decoloured **TzTz-POP-3** was subjected to SEM imaging and did not found any noticeable change in the morphology (Figure S21 in the Supporting Information). Similarly, from N_2 adsorption analysis, we got the BET value of 466 m^2g^{-1}. The decrease in surface area compared to the pristine **TzTz-POP-3** (604 m^2g^{-1}) could be attributed to some trapped dye molecules remaining inside the pores (Figure S22 in the Supporting Information). Nevertheless, upon repeating the dye adsorption cycle it has been found that the adsorption capacity of **TzTz-POP-3** towards FL was maintained with a slower rate and with a value of ~73% after 5 min. and further reached to 98.9% in 15 min. (Figure S23 in the Supporting Information). This result indicates that the reusability of **TzTz-POP-3** for multiple dye adsorption cycles could be possible.

Conclusions

In summary, the effects of tailoring substituents on TzTz formation have been studied using model compounds. On the way, an unprecedented stable intermediate compound (**TzTz-M3-I**) was isolated and characterized, which could be interesting for the understanding of TzTz formation to design TzTz-linked compounds and materials. Besides, we have also synthesized three novel, thermo-chemically stable TzTz-linked POPs with a variety of functional building units employing our one-pot catalyst-free strategy. All three synthesized TzTz-POPs possess very good chemical and thermal stability with excellent porosities. Interestingly, due to presence of multiple active anchoring sites coupled with permanent porosity, **TzTz-POP-3** showed a great potential for effective chemoselective removal of dye Fluorescein (FL) from a mixture with Parafuchsin (FU) in aqueous solution with an excellent selectivity of 1: 7. Overall, we believe that the presented understanding on TzTz formation, their integration to POPs synthesis and selective adsorption studies would inspire and pave a pathway for the further development of novel porous adsorbent materials based on heterocyclic linkages. As a prospect, we would like to note that various metal ions could also be anchored to TzTz-POPs for their application in photo/electrochemical catalysis such as Oxygen Reduction Reaction (ORR) and Hydrogen Evolution Reaction (HER) in the future.

Experimental Section

Synthesis of TzTz-POP-3: A Pyrex tube (o.d. × i.d. = 1 × 0.8 cm^2 and length 18 cm) was charged with 1,3,5-tris(4-formylphenyl)benzene (30 mg, 76.84 µmol, 1 eq.), dithiooximide (DTO) (13.8 mg, 115.26 µmol, 1.5 eq.) and 2 ml of nitrobenzene. This mixture was sonicated for 10 min. in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and then heated at 150 ºC for 4 days. A brownish yellow colored precipitate was collected by filtration and washed with ethanol, N,N'-dimethylacetamide (DMAc) and acetone several times until the filtrate became colorless, dried at 150 ºC under vacuum for 12 h to obtain the title porous polymer **TzTz-POP-3** (36 mg) in 82% isolated yield.

Synthesis of TzTz-POP-4: A Pyrex tube (o.d. × i.d. = 1 × 0.8 cm^2 and length 18 cm) was charged with 1,3,6,8-tetra(4-formylphenyl)pyrene (30 mg, 48.33 µmol, 1 eq.), DTO (11.6 mg, 96.67 µmol, 2 eq.) and 2 ml of N,N'-dimethylformamide (DMF). This mixture was sonicated for 10 min. in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and heated at 150 ºC for 4 days. After cooling the precipitate was collected by filtration and washed with ethanol, dichloromethane (DCM), DMAc and acetone several times until the filtrate became colorless, dried at 150 ºC under vacuum for 12h to provide targeted **TzTz-POP-4** (32 mg) in 76% isolated yield as yellow solid.

Synthesis of TzTz-POP-5: A Pyrex tube (o.d. × i.d. = 1 × 0.8 cm^2 and length 18 cm) was charged with tetra(4-fromyl-3-hydroxyphenyl)methane (30.2 mg, 41.60 µmol, 1 eq.), DTO (10 mg, 83.22 µmol, 2 eq.) and 2 ml of N,N'-dimethylformamide. This mixture was sonicated for 10 min. in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and then heated at 150 ºC for four days. A black-brown jelly material formed was collected and washed with ethanol, dichloromethane, DMAc and acetone several times until the filtrate became colorless, dried at 150 ºC under vacuum for 12h to provide targeted **TzTz-POP-5** (31 mg) as solid material in 77% isolated yield.

Chemoselective dye adsorption study: All the dye adsorption experiments were conducted at room temperature. Initial dye concentrations [FL and FU] were fixed to be ~50 µmol in Milli-Q water. Typically, 5 mg of **TzTz-POP-3** was added into 5 ml of dye solution, and the mixture was stirred with a magnetic stir bar at room temperature at a stirring rate of 500 r.p.m. At appropriate time intervals (see the result section), the mixture was filtered over Whatman PTFE 0.45 µm membrane filters. The concentration of dye in the filtrate was detected using an Agilent Cary 5000 UV-vis-NIR spectrophotometer. The removal efficiency of dye was calculated according to the following equation (1):

$$\text{Removal efficiency (\%)} = (C_0 - C) / C_0 \times 100 \quad (1)$$

where, C_0 and C are the concentrations of dyes at initial condition and in the filtrate, respectively. The dye adsorption experiments were performed 3 times to ensure the reproducibility and the best result has been used. The chemoselective dye adsorption study was performed using **TzTz-**

POP-3 as an adsorbent exactly as described above but with 1: 1 dye (FU: FL) as starting feed. The amount of adsorbed molecules was determined by HPLC-MS using an Agilent 1260 liquid chromatograph coupled to an Agilent 6538 ESI-Q-TOF mass spectrometer. For separation, an Agilent Zorbax Extend C18 column was used (2.1 x 50 mm; 1.8 Micron). The sample injection volume was 5 µl, and the flow rate was 0.3 ml min^{-1}. The mobile phase gradient started at 95% water with 0.1% formic acid and 5% methanol and rised up to 100% methanol in 10 mins. The mass spectra were recorded in the positive ion mode with nitrogen as drying gas (12 L min^{-1} at 350 ºC) using the following conditions: nebulizer 50 psig, VCap 4000 V, fragmentor 100 V, skimmer 45 V, mass range m/z 60 – 1000, scan rate 2 scans s^{-1}. The LC calibration curve was created for quantitative analysis using a 1:1 mixture (~50 µmol L^{-1} of FU and FL each), diluted to 80, 60, 40, 20 and 10%. The peak area of the extracted ions of the protonated molecules was used for quantification.

Conflict of Interest

There are no conflicts to declare.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 696656 (Graphene Flagship) and was supported financially bythe Center for Advancing Electronics Dresden (cfaed), the European Social Fund, and the Federal State of Saxony (ESF-Project "GRAPHD", TU Dresden). We thank Dr. Tilo Lübken for NMR measurements in solution, Mr. Hafeesudeen Sahabudeen for TEM measurements. We also acknowledge Dr. Junzhi Liu and Dr. Renhao Dong for helpful discussions. JJW thanks the DFG for funding a diffractometer (INST269/618-1).

Keywords: porous organic polymers • thiazolo[5,4-*d*]thiazole • microporous materials • molecular shieving • water treatment

[1] a) X. Zou, H. Ren, G. Zhu, *Chem. Commun.*, **2013**, *49*, 3925-3936; b) M. G. Schwab, M. Hamburger, X. Feng, J. Shu, H. W. Spiess, X. Wang, M. Antonietti, K. Müllen, *Chem. Commun.*, **2010**, *46*, 8932-8934; c) Z. S. Wu, L. Chen, J. Liu, K. Parvez, H. Liang, J. Shu, H. Sachdev, R. Graf, X. Feng, K. Müllen, *Adv. Mater.,* **2014**, *26*, 1450-1455.

[2] R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.*, **2012**, *37*, 530-563.

[3] a) H. Bildirir, J. P. Paraknowitsch, A. Thomas, *Chem. Eur. J.*, **2014**, *20*, 9543-9548; b) X. Zhuang, D. Gehrig, N. Forler, H. Liang, M. Wagner, M. R. Hansen, F. Laquai, F. Zhang, X. Feng, *Adv. Mater.,* **2015**, *27*, 3789-3796.

[4] X. Yang, S. Yao, M. Yu, J. X. Jiang, *Macromol. Rapid Commun.*, **2014**, *35*, 834-839.

[5] C. Gu, N. Huang, Y. Chen, L. Qin, H. Xu, S. Zhang, F. Li, Y. Ma, D. Jiang, *Angew. Chem. Int. Ed.*, **2015**, *54*, 13594-13598.

[6] a) L. Zou, D. Feng, T. F. Liu, Y. P. Chen, S. Fordham, S. Yuan, J. Tian, H. C. Zhou, *Chem. Commun.*, **2015**, *51*, 4005-4008; b) Y. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi, F. –S. Xiao, *Nano Today* **2009**, *4*, 135-142; c) F. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng, F. -S. Xiao, *J. Am. Chem. Soc.* **2012**, *134*, 16948-16950; d) Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F. –S. Xiao, *J. Am. Chem. Soc.* **2015**, *137*, 5204-5209.

[7] S. Kandambeth, B. P. Biswal, H. D. Chaudhari, K. C. Rout, H. S. Kunjattu, S. Mitra, S. Karak, A. Das, R. Mukherjee, U. K. Kharul, R. Banerjee, *Adv. Mater.*, **2017**, *29*, 1603945.

[8] Z. Chang, D. S. Zhang, Q. Chen, X. H. Bu, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 5430-5442.

[9] W. Wang, Y. Yuan, F.-X. Sun, G.-S. Zhu, *Chin. Chem. Lett.*, **2014**, *25*, 1407-1410.

[10] S. Dalapati, S. Jin, J. Gao, Y. Xu, A. Nagai, D. Jiang, *J. Am. Chem. Soc.*, **2013**, *135*, 17310-17313.

[11] L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong, D. Jiang, *J. Am. Chem. Soc.*, **2014**, *136*, 9806-9809.

[12] Y. Zhang, S. N. Riduan, *Chem. Soc. Rev.*, **2012**, *41*, 2083-2094.

[13] J. Cruz-Huerta, D. Salazar-Mendoza, J. Hernandez-Paredes, I. F. Hernandez Ahuactzi, H. Hopfl, *Chem. Commun.*, **2012**, *48*, 4241-4243.

[14] X. Ding, H. Li, Y.-C. Zhao, B.-H. Han, *Polym. Chem.*, **2015**, *6*, 5305-5312.

[15] J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao, D. Jiang, *Nat. Commun.*, **2013**, *4*, 2736.

[16] B. Li, Z. Guan, X. Yang, W. D. Wang, W. Wang, I. Hussain, K. Song, B. Tan, T. Li, *J. Mater. Chem. A*, **2014**, *2*, 11930.

[17] K. Dey, M. Pal, K. C. Rout, S. Kunjattu H, A. Das, R. Mukherjee, U. K. Kharul, R. Banerjee, *J. Am. Chem. Soc.*, **2017**, *139*, 13083-13091.

[18] Y.-C. Zhao, D. Zhou, Q. Chen, X.-J. Zhang, N. Bian, A.-D. Qi, B.-H. Han, *Macromolecules*, **2011**, *44*, 6382-6388.

[19] A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science*, **2005**, *310*, 1166-1170.

[20] B. P. Biswal, S. Chandra, S. Kandambeth, B. Lukose, T. Heine, R. Banerjee, *J. Am. Chem. Soc.*, **2013**, *135*, 5328-5331.

[21] a) S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine, R. Banerjee, *J. Am. Chem. Soc.*, **2012**, *134*, 19524-19527; b) A. I. Cooper, *CrystEngComm*, **2013**, *15*, 1483; c) L. A. Baldwin, J. W. Crowe, D. A. Pyles, P. L. McGrier, *J. Am. Chem. Soc.*, **2016**, *138*, 15134-15137.

[22] a) A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding, D. Jiang, *Nat. Commun.*, **2011**, *2*, 536; b) R. Dawson, A. I. Cooper, D. J. Adams, *Prog. Polym. Sci.*, **2012**, *37*, 530-563.

[23] a) F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, *J. Am. Chem. Soc.*, **2011**, *133*, 11478-11481; b) S. Q. Xu, R. R. Liang, T. G. Zhan, Q. Y. Qi, X. Zhao, *Chem. Commun.*, **2017**, *53*, 2431-2434; c) Y. Zhao, L. Guo, F. Gandara, Y. Ma, Z. Liu, C. Zhu, H. Lyu, C. A. Trickett, E. A. Kapustin, O. Terasaki, O. M. Yaghi, *J. Am. Chem. Soc.*, **2017**, *139*, 37, 13166-13172.

[24] F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 4570-4571.

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

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

[27] Z. Xiang, Y. Xue, D. Cao, L. Huang, J. F. Chen, L. Dai, *Angew. Chem. Int. Ed.*, **2014**, *53*, 2433-2437.

[28] Y. Xu, S. Jin, H. Xu, A. Nagai, D. Jiang, *Chem. Soc. Rev.*, **2013**, *42*, 8012-8031.

[29] D. Bevk, L. Marin, L. Lutsen, D. Vanderzande, W. Maes, *RSC Adv.*, **2013**, *3*, 11418-11431.

[30] J. Y. Jung, M. Kang, J. Chun, J. Lee, J. Kim, J. Kim, Y. Kim, S. J. Kim, C. Lee, J. Yoon, *Chem. Commun.*, **2013**, *49*, 176-178.

[31] A. N. Woodward, J. M. Kolesar, S. R. Hall, N. A. Saleh, D. S. Jones, M. G. Walter, *J. Am. Chem. Soc.*, **2017**, *139*, 8467-8473.

[32] M. G. Rabbani, A. K. Sekizkardes, O. M. El-Kadri, B. R. Kaafarani, H. M. El-Kaderi, *J. Mater. Chem.*, **2012**, *22*, 25409.

[33] X. Zhu, C. Tian, T. Jin, J. Wang, S. M. Mahurin, W. Mei, Y. Xiong, J. Hu, X. Feng, H. Liu, S. Dai, *Chem. Commun.*, **2014**, *50*, 15055-15058.

[34] R. O. Alves de Lima, A. P. Bazo, D. M. Salvadori, C. M. Rech, D. de Palma Oliveira, G. de Aragao Umbuzeiro, *Mutat. Res.*, **2007**, *626*, 53-60.

[35] V. K. Gupta, T. A. Saleh, *Environ. Sci. Pollut. Res. Int.*, **2013**, *20*, 2828-2843.

[36] a) E. T. Shamkhy, I. H. T. Al-Karkhi, E. A. Jaffar Al-Mulla, *Res. Chem. Intermed.*, **2012**, *39*, 2463-2471; b) R. C. Knighton, A. J. Hallett, B. M. Kariuki, S. J. A. Pope, *Tetrahedron Lett.*, **2010**, *51*, 5419-5422; c) L. K. Papernaya, A. A. Shatrova, I. V. Sterkhova, G. G. Levkovskaya, I. B. Rozentsveig, *Russ. J. Org. Chem.,* **2015**, *51*, 373-377.

[37] D. Li, Z. Zhang, S. Zhao, Y. Wang, H. Zhang, *Dalton Trans.*, **2011**, *40*, 1279-1285.

[38] J. A. Zampese, F. R. Keene, P. J. Steel, *Dalton Trans.*, **2004**, 4124-4129.

[39] D. Li, Y. Yuan, H. Bi, D. Yao, X. Zhao, W. Tian, Y. Wang, H. Zhang, *Inorg. Chem.*, **2011**, *50*, 4825-4831.

[40] ACD/C+H NMR Predictors and DB **2017**.1.3, *Advanced Chemistry Development*, Inc., Toronto, ON, Canada, www.acdlabs.com, **2017**.

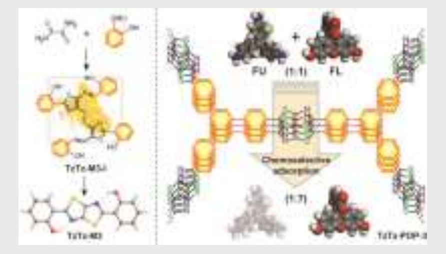
[41] a) H.-J. Zhang, J.-H. Wang, Y.-H. Zhang, T.-L. Hu, *J. Polym. Sci. A*, **2017**, *55*, 1329-1337; b) 2. Y. He, T. Xu, J. Hu, C. Peng, Q. Yang, H. Wang, H. Liu, *RSC Adv.*, **2017**, *7*, 30500-30505.

[42] K. Egbaria, M. Friedman, *Pharm Res.* **1992**, *9(5)*, 629-635.a) M. Seredych, T. J. Bandosz, *Ind. Eng. Chem. Res.* **2007**, *46,* 1786-1793; b) X. Zhang, L. Shi, G. Xu, C. Chen, *J. Incl. Phenom. Macrocycl. Chem.*, **2013**, *75*, 147–153.

[43] G. H. Ning, Z. Chen, Q. Gao, W. Tang, Z. Chen, C. Liu, B. Tian, X. Li, K. P. Loh, *J. Am. Chem. Soc.*, **2017**, *139*, 8897-8904.

FULL PAPER

Three novel, thermo-chemically stable TzTz-linked POPs, namely **TzTz-POP-3**, **TzTz-POP-4**, and **TzTz-POP-5** have been synthesized. Interestingly, the integrated TzTz moiety of the represented **TzTz-POP-3** renders chemoselective removal of organic dye Fluorescein (FL) from a mixture with Parafuchsin (FU) in aqueous solution. The **TzTz-POP-3** offered excellent chemoselectivity of ~1: 7 (FL: FU), compared to alike porous materials demonstrated for similar applications due to the presence of multiple active anchoring sites coupled with permanent porosity and appropriate pore window.



Bishnu P. Biswal, Daniel Becker, Naisa Chandrasekhar, Jensheer Shamsudeen Seenath, Silvia Paasch, Susanne Machill, Felix Hennersdorf, Eike Brunner, Jan J. Weigand, Reinhard Berger, Xinliang Feng**

Page No. 1 – Page No. 8

Title

Exploration of Thiazolo[5,4-*d*]thiazole Linkages in Conjugated Porous Organic Polymers for Chemoselective Molecular Sieving