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## Cascade synthesis of bis-*N*-sulfonylcyclobutenes via Cu(I)/Lewis acid-catalyzed (3 + 2)/(2 + 2) cycloadditions: observation of aggregation-induced emission enhancement from restricted C=N photoisomerization†

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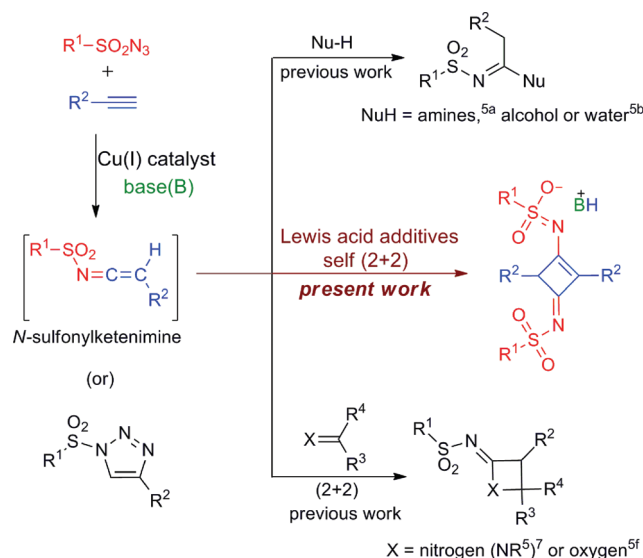
A remarkable role of Lewis acid additives in syntheses of bis-*N*-sulfonylcyclobutenes via copper(i) catalyzed (3 + 2)/(2 + 2) cycloaddition cascade of sulfonyl azides and terminal alkynes is described. In addition, these cyclobutenes display a unique aggregation-induced emission enhancement (AIEE), reported for the first time, arising predominantly from restricted rotation in C=N photoisomerization in the solid state.

Synthetic strategies involving cascade or domino reaction sequences that enable the construction of diverse and complex molecular architectures, in particular, those functionalized with variety of heteroatoms, present interesting and demanding challenges for the art of organic synthesis.<sup>1</sup> Cycloaddition cascades<sup>2</sup> are especially appealing by virtue of their ability to generate multiple C–C and/or C–heteroatom bonds with exquisite stereochemical control. For example, *N*-sulfonylketenimine, a key intermediate generated *in situ* from sulfonyl azides and terminal alkynes via copper catalyzed azide–alkyne cycloaddition process,<sup>3</sup> reported by Fokin and Meldal, has been utilized for a variety of multicomponent cascade reactions.<sup>4,5</sup>

Recently, we have developed an efficient one-pot synthesis of imidazolidin-4-ones via *N*-sulfonylketenimine, generated *in situ* from copper catalyzed cycloaddition of sulfonyl azides and terminal alkynes.<sup>6</sup> During the course of our investigation on further reactions of *N*-sulfonylketenimines we found that, in the absence of other nucleophiles,<sup>7</sup> 4-toluenesulfonyl chloride enhances the self (2 + 2) cycloaddition of *N*-sulfonylketenimines generated *in situ* from copper catalyzed (3 + 2) cycloaddition of tosyl azide and phenylacetylene in the presence of triethylamine (TEA) in dichloromethane (DCM) (Scheme 1). Interestingly, the cycloadduct is obtained as an ion pair namely triethylammonium-(*E*)-*N*-2,4-diphenyl-3-(tosylimino)cyclobut-1-enyl-4-methylbenzenesulfonimide, instead of the anticipated cyclobutenylsulfonamide. The structure and stereochemistry of the product are

unambiguously confirmed by single crystal X-ray analysis (Fig. 1), which are in accordance with the <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectral data (see ESI†). Herein we report the copper/Lewis acid catalyzed cycloaddition cascade of substituted sulfonyl azides and terminal alkynes to variety of highly substituted bis-*N*-sulfonylcyclobutenes under mild reaction conditions. Details of optimization of reaction parameters are given in Table 1.

Encouraged by the initial success using tosyl chloride as a Lewis acid additive, various acid chlorides and metal halides were tested (Table 1, entries 1–5). More promising results were obtained with benzoyl chloride, leading to improved yields of bis-*N*-sulfonylcyclobutenes and this was chosen for the remaining optimization studies. The source of additive was found to be critical for the transformation to proceed (Table 1, entry 6). Similarly without a copper source, there was no reaction (Table 1, entry 13) and this clearly highlights the specific role of copper(i) in the (3 + 2) cycloaddition of sulfonyl azides and alkynes. The use of CuCl or CuBr as alternate copper sources offered lower yields (Table 1, entries 7 and 8). However, our interest in

Scheme 1 Generation and reactivity of *N*-sulfonylketenimine

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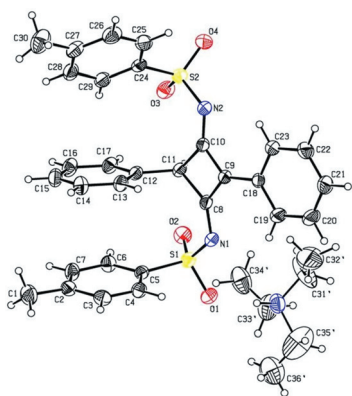
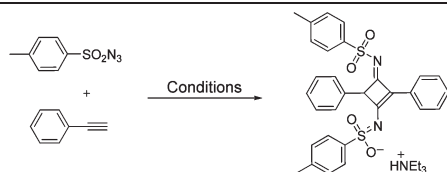


Fig. 1 Single crystal X-ray crystal structure of compound **3a**.

Table 1 Optimization of reaction conditions for the synthesis of triethylammonium-(*E*)-*N*-2,4-diphenyl-3-(tosylimino)cyclobut-1-enyl-4-methylbenzenesulfonimidate<sup>a</sup>



| Entry | Catalyst | Additive          | Solvent | Yield <sup>b</sup> (%) |
|-------|----------|-------------------|---------|------------------------|
| 1     | CuI      | TsCl              | DCM     | 66                     |
| 2     | CuI      | PhCOCl            | DCM     | 74                     |
| 3     | CuI      | 4-ClPhCOCl        | DCM     | 71                     |
| 4     | CuI      | AlCl <sub>3</sub> | DCM     | 56                     |
| 5     | CuI      | SbCl <sub>3</sub> | DCM     | 63                     |
| 6     | CuI      | —                 | DCM     | 09                     |
| 7     | CuBr     | PhCOCl            | DCM     | 62                     |
| 8     | CuCl     | PhCOCl            | DCM     | 59                     |
| 9     | Cu(i)-Y  | PhCOCl            | DCM     | 81                     |
| 10    | Cu(i)-Y  | PhCOCl            | Toluene | 63                     |
| 11    | Cu(i)-Y  | PhCOCl            | THF     | 68                     |
| 12    | Cu(i)-Y  | PhCOCl            | ACN     | 65                     |
| 13    | —        | PhCOCl            | DCM     | —                      |

<sup>a</sup> Reaction conditions: sulfonamide (1 mmol), alkyne (1 mmol), TEA (2 mmol), catalyst (20 mg), additive (20 mol%) solvent (2 ml), rt, N<sub>2</sub>, 30 minutes. <sup>b</sup> Isolated yield.

heterogeneous catalysis,<sup>8</sup> prompted us to use Cu(i)-modified zeolites (Cu(i)-Y), as a heterogeneous copper source, which was prepared according to a reported solid-state exchange procedure and characterized by powder XRD, XPS and EDX (see ESI†). Cu(i)-Y was found to be a better catalyst than other copper sources and offered the highest yield (Table 1, entry 9). Among the various solvents used (Table 1, entries 1, 10–12), DCM provided higher yield. Thus, the optimal conditions for this cycloaddition cascade involve Cu(i)-modified zeolite as a catalyst, benzoyl chloride as a Lewis acid additive<sup>9</sup> and TEA as base in DCM under N<sub>2</sub> atmosphere for 30 minutes (Table 1, entry 9).

This copper catalyzed cascade pathway is successfully extended to different combinations of sulfonamide and terminal alkynes. As depicted in Table 2, this reaction works very well for a wide range of substrates in short reaction times (30 minutes) at room temperature, and the corresponding bis-*N*-

Table 2 Copper(i)-Y zeolite catalyzed cascade synthesis of bis-*N*-sulfonylcyclobutenes<sup>a</sup>

| Entry | R <sup>1</sup>  | R <sup>2</sup>  | Yield <sup>b</sup> (%) |
|-------|---|---|------------------------|
| 1     | 4-MeC <sub>6</sub> H <sub>4</sub> ( <b>1a</b> )               | Ph ( <b>2a</b> )  | <b>3a</b> , 81         |
| 2     | Ph ( <b>1b</b> )  | <b>2a</b>   | <b>4a</b> , 79         |
| 3     | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <b>1c</b> ) | <b>2a</b>   | <b>3b</b> , 71         |
| 4     | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <b>1d</b> ) | <b>2a</b>   | <b>3c</b> , 80         |
| 5     | 4-ClC <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )               | <b>2a</b>   | <b>3d</b> , 77         |
| 6     | 4-BrC <sub>6</sub> H <sub>4</sub> ( <b>1f</b> )               | <b>2a</b>   | <b>4b</b> , 60         |
| 7     | 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>1g</b> ) | <b>2a</b>   | <b>4c</b> , 74         |
| 8     | 2-Naphthyl ( <b>1h</b> )                                      | <b>2a</b>   | <b>3e</b> , 85         |
| 9     | Methanesulfonyl ( <b>1i</b> )                                 | <b>2a</b>   | 0                      |
| 10    | <b>1a</b>   | 4-Pentyl C <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )          | <b>4d</b> , 70         |
| 11    | <b>1b</b>   | <b>2b</b>   | <b>4e</b> , 69         |
| 12    | <b>1h</b>   | <b>2b</b>   | <b>4f</b> , 71         |
| 13    | <b>1b</b>   | 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>2c</b> ) | <b>4g</b> , 64         |
| 14    | <b>1e</b>   | <b>2c</b>   | <b>3f</b> , 61         |
| 15    | <b>1h</b>   | <b>2c</b>   | <b>3g</b> , 66         |
| 16    | <b>1a</b>   | n-Hexyl ( <b>2d</b> )   | 0                      |
| 17    | <b>1a</b>   | Cyclopropyl ( <b>2e</b> )                                     | 0                      |

<sup>a</sup> Reaction conditions: sulfonamide (1 mmol), alkyne (1 mmol), TEA (2 mmol), Cu(i)-zeolite (20 mg), PhCOCl (0.2 mmol), DCM (2 mL), rt, N<sub>2</sub>, 30 minutes. <sup>b</sup> Isolated yield.

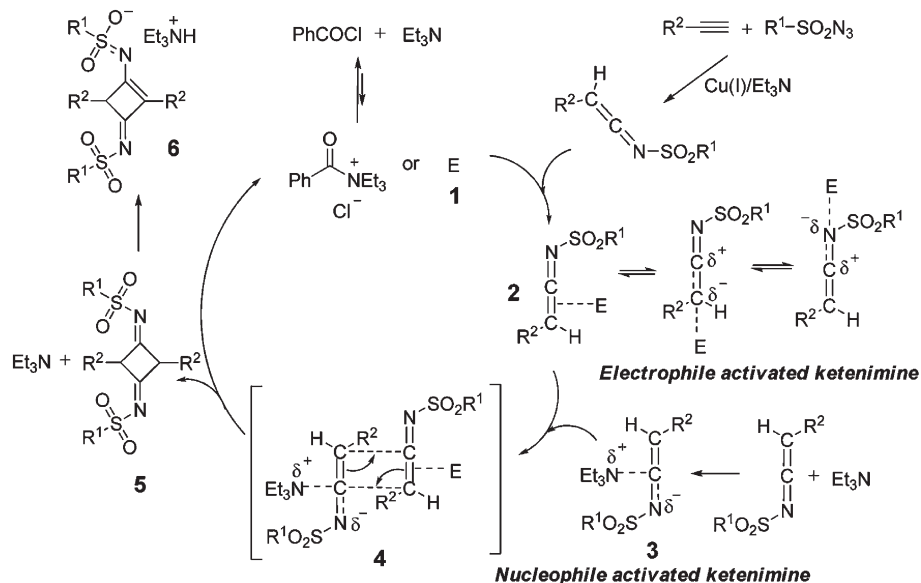
Table 3 Reusability of Cu(i)-Y in the cascade synthesis of bis-*N*-sulfonylcyclobutenes<sup>a</sup>

| Reuse              | 1st | 2nd | 3rd | 4th |
|--------------------|-----|-----|-----|-----|
| Yield <sup>b</sup> | 81  | 78  | 72  | 65  |

<sup>a</sup> Reaction conditions: tosyl azide (5 mmol), phenylacetylene (5 mmol), benzoyl chloride (1 mmol), TEA (6 mmol), Cu(i)-Y (100 mg), solvent (8 mL), rt, N<sub>2</sub>, 30 minutes. <sup>b</sup> Isolated yield.

sulfonylcyclobutenes are obtained in fairly good yields. In most of the cases, the products are purified by recrystallization and are obtained as triethylammonium salts (**3**). Interestingly, wherever purification by column chromatography (silica gel) is performed, the product is obtained as an amide (**4**). Substituted arylsulfonamide azides and arylacetylenes, containing electron-withdrawing groups as well as electron-donating groups are well tolerated in this reaction. In contrast, with an aliphatic sulfonamide or aliphatic alkynes, there is no product formation (Table 2, entries 9, 16 and 17). The reason may be the absence of stabilizing intramolecular aromatic  $\pi$ - $\pi$  stacking interactions in the aliphatic starting materials. Meanwhile, the recovery and reuse of Cu(i)-Y are also investigated, and the recovered catalyst exhibits good activity up to 4 consecutive cycles (Table 3).

In the proposed mechanism (Scheme 2), benzoyl chloride added in catalytic amount (0.2 mmol), combines with triethylamine (present in excess, 2 mmol) to form benzoyltriethylammonium chloride as the catalytic electrophilic species (E, **1**).



Scheme 2 Proposed mechanistic pathway.

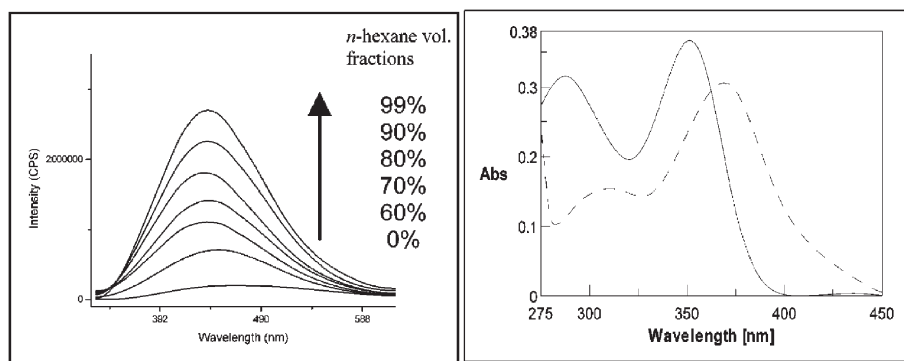


Fig. 2 (a) PL spectra of **3a** in different n-hexane-CHCl<sub>3</sub> ratios at a concentration of  $7 \times 10^{-6}$  M, excited at 350 nm (b) UV-visible absorption spectra of **3a** in CHCl<sub>3</sub> solution ( $7 \times 10^{-5}$  M, black line) and in n-hexane-CHCl<sub>3</sub> (99 : 1) mixture ( $7 \times 10^{-5}$  M, dotted line).

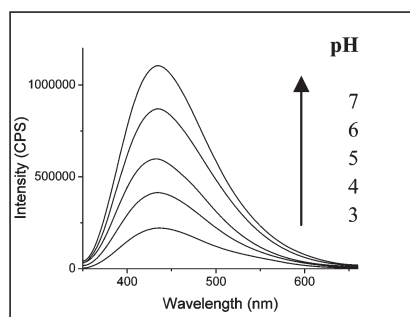
This activates the *in situ* generated ketenimine to form an intermediate **2**. Simultaneously, the excess TEA, acting as a nucleophile, polarizes another molecule of ketenimine to form **3**. Consequent (2 + 2) cycloaddition between these two electrophile as well as nucleophile activated ketenimine generates the cyclobutane **5** and releases the active electrophile E for subsequent cycloadditions. The [2 + 2] dimer, **5**, readily combines with TEA forming the more stable triethylammonium imidate **6**, with extended conjugation, being the driving force for salt formation.

Aggregation-induced emission enhancement (AIE/AIEE) has turned out to be the one of the most intriguing phenomena<sup>10</sup> to achieve solid-state luminescent materials, with optoelectronic applications, and also as highly selective chemosensors and bio-imaging applications.<sup>11</sup> This aspect of AIEE-active materials primarily resolves the problem of fluorescence quenching resulting from aggregation. Possible reasons for this AIEE are formation of specific *J*-aggregates in the solid state and either single or combined effect of, restricted intramolecular rotation (RIR) of C-C, C-N or N-N single bond and C=C double bond as well as molecular planarization. To have a better understanding of this phenomenon and also to develop novel applications,

extensive efforts are being made to achieve new AIEE active molecules by various research groups.<sup>12</sup>

In molecules with an unbridged C=N structure, C=N isomerization is the predominant decay process of excited states and so those compounds are often non-fluorescent. In contrast, the fluorescence of their covalently bridged analogs increases dramatically due to the suppression of C=N isomerization in the excited state. A variety of fluorescent chemosensors with Schiff base structures have been developed and restriction of C=N isomerization is responsible for the sensing mechanism.<sup>13</sup> To our surprise, the synthesized bis-*N*-sulfonylcyclobutenes (**3**) of the present study are found to exhibit AIEE involving C=N photoisomerization and also a strong pH dependent fluorescence. To the best of our knowledge, restricted C=N photoisomerization as a source behind an AIEE system is unprecedented.

To study the AIEE phenomenon of the synthesized cyclobutenes in detail, we investigated the UV-Vis absorption and emission behaviours of **3a** and **3e**, as selected examples. Both are soluble in CHCl<sub>3</sub>, acetone, DMF, and DCM, but are insoluble in n-hexane and water. **3a** displays two distinct absorption bands at 280 and 350 nm in CHCl<sub>3</sub> medium (Fig. 2b). Based on, DFT

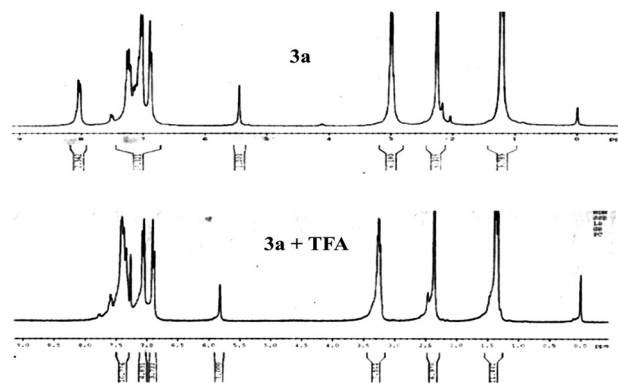


**Fig. 3** PL spectra of **3a** ( $5 \times 10^{-5}$  M) at different pH values in an acetone–water (60 : 40) buffer excited at 350 nm.

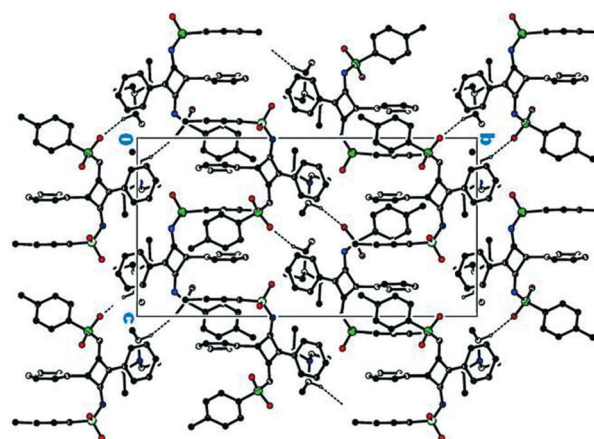
(B3LYP/6-31G) calculations, the band at 350 nm is assigned to the ( $\pi$ - $\pi^*$ ) of HOMO of diimine functionalized cyclobutene core and LUMO of sulfonylaryl ring (Fig. g and h, ESI†). Stable n-hexane dispersions of aggregates of **3a/3e** are prepared using  $\text{CHCl}_3$  as an n-hexane-miscible solvent. Fig. 2a shows the corresponding emission spectra of **3a** in  $\text{CHCl}_3$  ( $\lambda_{\text{exi}} = 350$  nm) with different n-hexane– $\text{CHCl}_3$  ratios at a concentration of  $7 \times 10^{-6}$  mol. Initially, the emission from the solution of **3a** in  $\text{CHCl}_3$  is so weak that almost no photoluminescence (PL) signal is noticed. However, a solution containing 70 : 30 (v/v) n-hexane– $\text{CHCl}_3$  mixture displays a dramatic enhancement of luminescence. When the n-hexane– $\text{CHCl}_3$  ratio reaches 99%, the emission intensity enhances very significantly with a regular shift towards the blue region (Fig. 2a). A similar increase in photoluminescence of **3e** upon addition of n-hexane to a  $\text{CHCl}_3$  solution is also observed (Fig. d, ESI†). The emission images of **3a** in pure  $\text{CHCl}_3$  and, 99 : 1 (v/v) n-hexane– $\text{CHCl}_3$  under UV light (365 nm) illumination at room temperature are shown in (Fig. e, ESI†). Evidently, the emission of these cyclobutenes is significantly enhanced in the solid state, indicating that, **3a** and **3e** are AIE-active. This is further supported by the observation of a red shift, due to strong intermolecular interactions (Fig. 2b), in the absorption spectra of **3a** (which is present as suspended particles in 99% n-hexane).

The fluorescence spectra of **3a** in the acetone–water mixture (60 : 40) as a function of pH were also investigated (Fig. 3), and display decreased intensity in acidic environment. This is attributed to protonation of imine groups which, in turn, reduces the electron density making it weakly fluorescent. This is further supported by  $^1\text{H}$  NMR data. To facilitate the effective overlap of  $\pi$ -orbitals, the central cyclobutene ring and the aryl ring (B) were oriented in the same plane (see crystal structure of **3a**, Fig. 1). Consequently, *ortho*-hydrogens of aryl ring (B) are placed very close to the imine nitrogens, shifted downfield and come to resonance at 8.05 ppm as a doublet. However, in the presence of trifluoroacetic acid (TFA), the deshielded *ortho* protons are shifted up field, which may be due to the out of the plane twisting of aryl ring (B) in the sterically hindered iminum salts (Fig. 4).

Single crystal X-ray analysis also provides evidence for the AIEE behaviour of **3a**. The bond lengths of both the imine groups ( $1.31 \text{ \AA}$ ) were found to be higher than the normal imines ( $1.27 \text{ \AA}$ ). This decrease in bond order from the normal value is attributed to the effective delocalization of electrons between the two sulfonyl groups at the opposite diagonals of



**Fig. 4**  $^1\text{H}$  NMR spectrum of **3a** and **3a** + TFA.



**Fig. 5** Molecular packing diagram of **3a**.

cyclobutenes. Consequently, we believe photoisomerization is easier, when compared to the normal unconjugated  $\text{C}=\text{N}$  double bonds and this becomes the major non-radiative channel of twisted intramolecular charge transfer (TICT) state in chloroform solution. In contrast, as evident from crystal packing diagram (Fig. 5), molecules are tightly packed in the solid state as a rigid supramolecular network. Consequently, the  $\text{C}=\text{N}$  photoisomerization is greatly slowed down in solid state and thus, **3a** in this aggregated state exhibits significantly enhanced fluorescence emission compared to its weak emission when molecularly dispersed in dilute solution.

In summary, a novel and efficient method was developed for the facile synthesis of bis-*N*-sulfonylcyclobutenes *via* copper(I)/ $\text{PhCOCl}$  catalyzed (3 + 2)/(2 + 2) cycloaddition cascade of sulfonyl azides and terminal alkynes in short reaction times. The use of a copper(I)-Y zeolite as a heterogeneous copper(I) source allows for the fast and easy isolation of the reaction products by simple filtration in addition to other advantages such as catalyst recyclability, ambient temperature and minimization of metallic wastes. The observed AIEE of is attributed to the restricted  $\text{C}=\text{N}$  photoisomerization in the aggregated state, based on preliminary optical spectral measurements and single crystal XRD data. To the best of our knowledge, this is the first report wherein AIE/AIEE is attributed to restriction of rotation in  $\text{C}=\text{N}$  photoisomerization, which is more pronounced in the solid state.

Further studies towards a deeper mechanistic understanding of this restricted rotation in C=N photoisomerization in the solid state with different entities with varying molecular crystal structures are under way.

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## Notes and references

- (a) L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115–136; (b) D. Enders, C. Grondal and M. R. M. Hüttl, *Angew. Chem.*, 2007, **119**, 1590–1601. D. Enders, C. Grondal and M. R. M. Hüttl, *Angew. Chem., Int. Ed.*, 2007, **46**, 1570–1581.
- (a) E. A. Anderson, *Org. Biomol. Chem.*, 2011, **9**, 3997–4006; (b) C. Grondal, M. Jeanty and D. Enders, *Nat. Chem.*, 2010, **2**, 167–178; (c) K. C. Nicolaou and J. S. Chen, *Chem. Soc. Rev.*, 2009, **38**, 2993–3009; (d) K. C. Nicolaou, D. J. Edmonds and P. G. Bulger, *Angew. Chem.*, 2006, **118**, 7292–7344. K. C. Nicolaou, D. J. Edmonds and P. G. Bulger, *Angew. Chem., Int. Ed.*, 2006, **45**, 7134–7186.
- (a) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596; (b) C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057.
- For recent reviews see: (a) S. H. Kim, S. H. Park, J. H. Choi and S. Chang, *Chem.-Asian J.*, 2011, **6**, 2618–2634; (b) P. Lu and Y.-G. Wang, *Synlett*, 2010, 165–173.
- Selected examples: (a) I. Bae, H. Han and S. Chang, *J. Am. Chem. Soc.*, 2005, **127**, 2038; (b) S. H. Cho, E. J. Yoo, I. Bae and S. Chang, *J. Am. Chem. Soc.*, 2005, **127**, 16046; (c) S. H. Cho and S. Chang, *Angew. Chem., Int. Ed.*, 2008, **47**, 2836–2839; (d) M. P. Cassidy, J. Raushel and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3154; (e) R. Husmann, Y. S. Na, C. Bolm and S. Chang, *Chem. Commun.*, 2010, **46**, 5494; (f) W. Yao, L. Pan, Y. Zhang, G. Wang, X. Wang and C. Ma, *Angew. Chem., Int. Ed.*, 2010, **122**, 9396; (g) W. Z. Song, M. Lei, Y. Shen, S. Cai, W. Lu, P. Lu and Y. G. Wang, *Adv. Synth. Catal.*, 2010, **352**, 2432–2436; (h) J. Wang, Y. Zhu, P. Lu and Y.-G. Wang, *Chem. Commun.*, 2011, **47**, 3275; (i) S. Li, Y. Luo and J. Wu, *Org. Lett.*, 2011, **13**, 4312.
- K. Namitharan and K. Pitchumani, *Org. Lett.*, 2011, **13**, 5728.
- Previously, during the synthesis of *N*-Sulfonylazetid-2-imines Whiting and Fokin observed the very slow dimerization of *N*-sulfonylketenimine as a side reaction in the absence of other nucleophiles; M. Whiting and V. Fokin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3157.
- (a) K. Namitharan and K. Pitchumani, *Eur. J. Org. Chem.*, 2010, 411; (b) K. Namitharan, M. Kumarraja and K. Pitchumani, *Chem.-Eur. J.*, 2009, **15**, 2755; (c) T. Subramanian and K. Pitchumani, *Catal. Sci. Technol.*, 2012, **2**, 296, DOI: 10.1039/c1cy00383f.
- Non-metal halides as Lewis acids: (a) B. Kaboudin and E. Jafari, *Synlett*, 2008, 1837; (b) R. Wong and S. J. Dolman, *J. Org. Chem.*, 2007, **72**, 3969; (c) J. Ciesielski, D. P. Canterbury and A. J. Frontier, *Org. Lett.*, 2009, **11**, 4374; (d) M. P. Jennings and K. B. Sawan, *Eur. J. Org. Chem.*, 2004, 3201.
- (a) J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) B.-K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410.
- (a) K. Walzer, B. Maennig, M. Pfeiffer and K. Leo, *Chem. Rev.*, 2007, **107**, 1233–1271; (b) L. S. Hung and C. H. Chen, *Mater. Sci. Eng., R*, 2002, **39**, 143–222; (c) D. Dini, *Chem. Mater.*, 2005, **17**, 1933–1945; (d) P. I. Shih, C. Y. Chuang, C. H. Chien, E. W. G. Diao and C. F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3141–3146; (e) Y. T. Lee, C. L. Chiang and C. T. Chen, *Chem. Commun.*, 2008, 217–219; (f) C. McDonagh, C. S. Burke and B. D. MacCraith, *Chem. Rev.*, 2008, **108**, 400–422; (g) D. Citterio, J. Takeda, M. Kosugi, H. Hisamoto, S. Sasaki, H. Komatsu and K. Suzuki, *Anal. Chem.*, 2007, **79**, 1237–1242; (h) D. T. Quang and J. S. Kim, *Chem. Rev.*, 2010, **110**, 6280–6301; (i) S. R. Meech, *Chem. Soc. Rev.*, 2009, **38**, 2922–34.
- For a recent review see: Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; Selected examples: (a) S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675–13683; (b) G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Z. Tang, D. B. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335–6346; (c) S.-J. Li, B.-K. An, S.-D. Jung, M.-A. Chung and S. Y. Park, *Angew. Chem., Int. Ed.*, 2004, **43**, 6346–6350; (d) Z. Xie, B. Yang, G. Cheng, L. Liu, F. He, F. Shen, Y. Ma and S. Liu, *Chem. Mater.*, 2005, **17**, 1287–1289; (e) J. W. Chung, Y. You, H. S. Huh, B. K. An, S. J. Yoon, S. H. Kim, S. W. Lee and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 8163–8172; (f) H. Tong, Y. Dong, M. Haussler, J. W. Y. Lam, H. H.-Y. Sung, I. D. Williams, J. Sun and B. Z. Tang, *Chem. Commun.*, 2006, 1133–1135; (g) H. Tong, Y. Dong, Y. Hong, M. Haussler, J. W. Y. Lam, H. H.-Y. Sung, X. Sun, J. Yu, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem. C*, 2007, **111**, 2287–2294.
- (a) J. S. Wu, W. M. Liu, X. Q. Zhuang, F. Wang, P. F. Wang, S. L. Tao, X. H. Zhang, S. K. Wu and S. T. Lee, *Org. Lett.*, 2007, **9**, 33–36; (b) V. Chandrasekhar, P. Bag and M. D. Pandey, *Tetrahedron*, 2009, **65**, 9876–9883; (c) Z. X. Li, M. M. Yu, L. F. Zhang, M. Yu, J. X. Liu, L. H. Wei and H. Y. Zhang, *Chem. Commun.*, 2010, **46**, 7169–7171.