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Anoop Kumar Saini,<sup>a</sup> Kaushik Natarajan<sup>b</sup> and Shaikh M. Mobin, \*<sup>a,b,c</sup>

A new multitalented azine ligand: elastic bending, single-crystal-

to-single-crystal transformation and a fluorescence turn–on Al(III)

We report a rare combination of two unique properties of azine based ligand (H<sub>3</sub>L): In a solid-sate crystalline material it shows highly flexible and elastic behavior which on triggering with light results slightly deviate with phase transformation at Single-Crystal-to-Single-Crystal (SCSC) level. Furthermore, in solution state it acts as a highly selective, sensitive and reversible Al<sup>3+</sup> sensor with the detection limit of 42 nM.

sensor

The design and synthesis of multi-tasking materials has attracted tremendous interest owing to their fascinating applications and economic viability.<sup>1</sup> Although individual properties of the material in the solid-state and the solution state have been explored enormously, reports on combined studies comprising of properties in both solid-state and in solution are sparse. In solid-state, crystalline materials are of paramount importance due to their potential applications in the mechanical actuators,<sup>2</sup> phototransistors,<sup>3,4</sup> light-emitting diodes (LEDs),<sup>5</sup> solar cells,<sup>6</sup> photonics and flexible electronics<sup>7,8</sup> etc. In addition, crystal engineering is a powerful tool that helps organize complex materials into well-disciplined crystalline lattices via self-assembly of functional molecules. In fact, the engineered crystals are dominant to supramolecular materials,<sup>9</sup> drug formulation,<sup>10</sup> artificial mechanosensors<sup>11</sup> and smart nanomaterials.<sup>12</sup> In crystal engineering, the major phenomena which attract attention are (i) the development of organic co-crystals (multi-component system), a prime focal point of pharmaceutical industries, (ii) single-crystal-to-singlecrystal (SCSC) transformations which involve several bond breaking and formation processes that leads to unusual products which may not be easily feasible by routine synthetic methods and currently (iii) investigation of bending properties crystals as introduced by Desiraju of et al. in hexachlorobenzene and further extensively explored by Naumov and Reddy et al. about their mechanical properties.13,14 All these features in crystal engineering are of high interest in the scientific community today.

Recently, mechanically flexible materials have gained much attention due to their promising application in pharmaceutical processes from formulation to tableting.<sup>15</sup> Generally, the flexibility of organic crystals depends on the mechanical force applied, which in turn depends on strong or weak interactions between lattice molecules. Most of the existing reports on bendable crystals are results of serendipity but lately Reddy et al. have reported a strategy for the design and synthesis of bendable crystals.<sup>8</sup> So far, the reports on elasticity and plasticity of molecular crystals have been revolving around the following synthons: polyhalogenated N-benzylideneanilines,<sup>16</sup> organic co-crystals,<sup>10</sup> ester spacer based molecules,<sup>15</sup> naphthalene diimides derivatives,<sup>8</sup> Schiff bases,<sup>16</sup> vanillin derivatives<sup>8</sup> and pyrimidine.<sup>17</sup> However, to the best of our knowledge, so far, no report is available on azine based elastic crystals. Due to the presence of flexible -C=N-N=C- azine unit, it is found that these crystals exhibit efficient internal stress dissipation, which is important for many applications involving flexible substrates.18

The recent upsurge in the field of SCSC transformation reveals that transformed newer materials via external stimuli like light, heat and vapor have significant applications in sensor technology and gas storage.<sup>19</sup> The reversible/irreversible SCSC transformations in MOF and metal complexes are well documented.<sup>20</sup> However, in organic ligands, the SCSC transformations are rare and mostly restricted to [2+2] cycloaddition of two neighboring olefinic bonds which are designed to be close to each other within the range of 3.6-5.00 Å via introduction of photo-induced strategy which has been extensively studied by MacGillivray and Vittal et al.<sup>21</sup> To the best of our knowledge only one report is available on light induced SCSC transformation of non-olefinic ligands.<sup>22</sup> Nevertheless, in solution state, the relatively free movement of molecules makes it convenient to explore a huge repository of properties. In particular, organic luminous and nonluminous molecules play an important role in optics, materials and biosciences.<sup>23</sup> The electronics. recent developments related to solution state have witnessed an enormous increase in the research areas of aggregation induced emission (AIE) and ion sensing.<sup>24-26</sup>

Herein, we attempt to explore a unique combination of both the crystalline solid-state properties that deals with the bending properties of crystals which undergo SCSC

<sup>&</sup>lt;sup>a</sup>Discipline of Chemistry, <sup>b</sup>Discipline of Metallurgy Engineering and Materials Science, Center for Biosciences and Bio-Medical Engineering, Indian Institute of

Technology Indore, Simrol, Khandwa Road, Indore 453552, India

<sup>\*</sup>corresponding author

Email: xray@iiti.ac.in

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transformation via light stimuli and further the solution state properties involving fluorescence turn ON for Al<sup>3+</sup> sensing.

A new multifunctional azine based ligand (H<sub>3</sub>L) was obtained by the reaction of synthesized (E)-3-(hydrazonomethyl)benzene-1,2-diol with 2-hydroxy-1napthaldehyde (1: 1) in methanol at room temperature for 15 h (Scheme 1). H<sub>3</sub>L has been characterized by NMR, ESI–MS and is further authenticated by single crystal X-ray studies. The TGA study indicates a two-step rapid decomposition of H<sub>3</sub>L at around 320°C and 630°C, while DSC studies show a two phase transitions at 197°C and 315°C (Fig. S1-S5).



# Scheme 1. Synthesis of H<sub>3</sub>L.

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 $H_{3}L$  crystallizes in monoclinic  $P2_{1}/n$  space group (Fig. S6, Table S1). Crystal structure of H<sub>3</sub>L reveals that naphthyl group and benzene 1,2 diol units separated by E/Z aldazine unit which are arranged in a same plane. Molecular crystals of H<sub>3</sub>L were grown in different solvents such as methanol, ethanol and acetonitrile in all these solvents the crystals of H<sub>3</sub>L were found to be elastically bendable in nature. A systematic evaluation of the bending characteristics of the crystal was carried out, based on methods previously described by Ghosh and Reddy.<sup>27</sup> This was demonstrated by simply bending the crystal from both the ends by using tweezer which on releasing it goes back to its original position (Supplementary video 1).

In order to confirm the elasticity of the  $H_3L$  crystal, with much efforts we mounted the crystal in bent position by entrapping the crystal in the Y-shaped designed glass capillary and recorded the diffraction patterns by employing SCXRD techniques. Despite being bent we were able to index the unit cell parameters, which come out to be same as that of normal crystal (Table S2). We observed a slight decay in the intensities of diffraction spots in the bent crystal as compared to normal crystal, which is attributed to modified absorption and reflection characteristics of the crystals due to a change in effective thickness of the crystal at the critical bending points during elastic bending or elongation<sup>28</sup> (Fig. S7). However, we could not solve the structure with this quality of very weak diffraction. This confirms that even at bent position the molecules are still intact in the lattice, thus retaining the crystallinity. Further, on relaxation the same crystal shows original unit cell. This provides strong indication for significant elastic stretching property of the crystal (Supplementary Video 2-4). The different elastic stages of the successive bending in the H<sub>3</sub>L crystal are shown in Fig 1.

Bending experiments have been performed on the H<sub>3</sub>L crystal. A model has been assumed wherein elastic bending introduces strain energy (Es) due to compression and stretching of outer and inner arcs, respectively. Interestingly, the thinner crystals can be bent to a greater extent compared to thicker crystals due to the fact that the thicker crystals experience a greater level of strain energy, as the magnitude of change in  $\Delta I$  (where I represents the length of the crystal) for inner and outer arcs will be greater for the same extent of bending.



Fig. 1 The different elastic stages in the successive bending (ai) in the H<sub>3</sub>L.

The Es will also be greater with a decrease in critical radius, as can be seen from continuum mechanics.<sup>29,30</sup> A simple calculation was performed to find out the values of  $\Delta I$  and critical radius r<sub>c</sub> for the H<sub>3</sub>L. The results of the calculations are explained in-depth in the supplementary information, while a schematic of the bending experiment along with the type of bending experienced by the crystal is represented in Fig. S8.

The average change in translation along the 1D axis ( $\Delta I$ ) is found to be 2.6743 Å/molecule for H<sub>3</sub>L crystal of 430 μm in length (0.43 mm). The calculation shows critical radius for breakage of the crystal, r<sub>c</sub>, was found to be 30.8 µm and the breaking strain is experienced on the crystal when the bending angular rotation per molecule is 0.0006134 °/molecule. The calculations for the bent and original crystal show only minimal changes, during or after bending. This serves as further proof for the earlier indications of significant and exceptional elasticity of H<sub>3</sub>L.The elastic nature of H<sub>3</sub>L may be due the tensile force between naphthyl and benzene diol groups through E/Z aldazine (-C=N-N=C-) unit followed by the attractive force from the van der Waals interactions.<sup>31</sup>

An earlier report by Barret et al.<sup>32</sup> demonstrating light driven bending of azobenzene crystals prompted us to explore the SCSC transformation of H<sub>3</sub>L crystal under the influence of light. In this regards, the crystal of H<sub>3</sub>L was exposed to UV irradiation, which resulted in the phase transformed crystal structure (H<sub>3</sub>L<sup>1</sup>). This SCSC transformation involved change in space group from  $P2_1/n$  in  $H_3L$  to C2/c in  $H_3L^1$  with approximately twice the length of the original a-axis (Table S1). The overlay molecular structure of H<sub>3</sub>L<sup>1</sup> shows deviation of 11.77° from H<sub>3</sub>L plane (Fig. 2a and 2b).



Fig. 2 (a) Packing diagram of H<sub>3</sub>L and H<sub>3</sub>L<sup>1</sup>. (b) Molecular overlay structure of H<sub>3</sub>L (blue) and H<sub>3</sub>L<sup>1</sup> (red).

Packing features of  $H_3L$  and  $H_3L^1$  shows the presence of intra and intermolecular H-bonding interactions. The

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intramolecular O-H···N interactions involves both the N atoms of an azine unit and the H atoms of hydroxy groups of naphthyl and diol unit (Fig. S9). The intermolecular O–H…O, interaction in H<sub>3</sub>L involves an H-atom of diol group and an O atom of adjacent diol group, O(3)-H(103)···O(3), 1.998(1) Å leading to the formation of dimer with single hand shake position. Further, each dimeric unit is connected to neighbouring dimer forming 1D-polymeric chain (Fig. S10 and Table S3). However, in H<sub>3</sub>L<sup>1</sup> an intramolecular interactions are between O and H atoms of diol group from one molecule to the H and O atoms of adjacent diol group, O(3)-H(103)···O(2), 2.106(9) forming a dimer with both hand in hand handshake position with additional C-H···O, H-bonding interaction between an O atom of napthyl unit and hydrogen atom of neighboring molecule,  $C(12)-H(12)\cdots O(1)$ , 2.602(13) Å, leading to the formation of 1D-polymeric chain (Fig. S11 and Table S3). This H-bonded 1D-polymeric chain structures suggest that relaxation processes are dominant which is favorable for elastic bending.<sup>33</sup> Moreover, other azine based ligands  $L_1$  and  $L_2$  in absence of -OH groups do not undergo photo-induced SCSC transformation (Scheme S1 and S2). It is observed that the intramolecular H(101)...N(1) and H(2)...N(2) distances in H<sub>3</sub>L are found to be 1.769(5) Å and 1.903(5) Å , respectively, whereas the similar intramolecular H(101)...N(1) and  $H(2) {\cdots} N(2)$  distances in  $H_3 L^1$  are found to be enhanced considerably, 1.830(5) Å and 1.927(3) Å, respectively (Fig. S9).

The SCSC transformation of  $H_{3}L$  to  $H_{3}L^{1}$  can be explain by the probable mechanistic pathways as shown in Scheme 2. In the first step, on exposure of  $H_3L$  to UV light the O-H…O hydrogen bonding interaction is cleaved (step 1) which brings two adjacent molecules very close to each other from approximately 5.642 Å to 2.806 Å but due to strong hindrance between two bulkier naphthyl unit, one of the molecule vertically flipped to 180°. Thus, the two adjacent molecules strongly bonded to each other via strong O-H…O interactions (step 2) and subsequently each dimeric unit is stabilized by C- $H \cdots O$  interactions resulting in packing features of  $H_3L^1$  as discussed above. Further, the bending properties of  $H_3L^1$ crystal was also explored which displayed same r<sub>c</sub> value with enhanced elastic property at a higher breaking strain of 0.001177 °/molecule as compared to H<sub>3</sub>L (Supplementary Video 5).

(Slice of the hydrogen bonded Step 1 Network in H<sub>3</sub>L) Vertical Flip (Packing diagram of H<sub>3</sub>L<sup>1</sup>) Step 2

Scheme 2. Proposed pathway for the transformation of H<sub>3</sub>L to H<sub>3</sub>L<sup>1</sup>.

After displaying excellent solid–state crystalline properties of  $H_{3}L$  and owing to its good solubility, we decided to investigate the solution state properties. Aluminum is the third most abundant element on the earth's crust with a variety of applications. The development of highly selective and sensitive sensors for the detection of aluminum ions is of great

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importance in biological assays and environmental monitoring due to potential health implications caused by sovecdoses of aluminium.<sup>34-36</sup>

The photophysical behavior of H<sub>3</sub>L was investigated via absorption and emission studies. The absorption spectra of H<sub>3</sub>L in acetonitrile (ACN) mixture (7:3 v/v in 10  $\mu$ M HEPES buffer at pH = 7.2) was dominated by two absorption peaks at 325 and 382 nm wavelength corresponding to the  $\pi$ - $\pi^*$  and n- $\pi^*$ transition, respectively. The subsequent addition of Al<sup>3+</sup> in the form of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O results in a gradual decrease of absorption maxima at 325 and simultaneously increases at 382 nm with an isosbestic point at 344 nm. This provides strong evidence for enhanced binding of H<sub>3</sub>L towards Al<sup>3+</sup> ion (Fig. S12). The emission spectra of H<sub>3</sub>L exhibit a weak fluorescence peak at 500 nm. The titration of H<sub>3</sub>L with Al<sup>3+</sup> resulted in a gradual enhancement in fluorescence intensity at 555 nm with 50 nm bathochromic shift (Fig. 3a). A plausible reason for the fluorescence turn on towards Al<sup>3+</sup> may be due to (i) the photo induced electron transfer (PET) suppressed by Al<sup>3+</sup> coordination and (ii) large bathochromic shift and (iii) isosbestic point appear in absorption spectrum.<sup>35</sup> Thus, the results obtained from absorption and emission studies clearly indicate that the sensing behavior of  $H_3L$  is specific to  $AI^{3+}$  ions. The limit of detection (LOD) was determined to be 42 nM and fluorescence response time was found to be 50 s (Fig. S13).

The selectivity test was also performed towards various metal ions with concentration four times the concentration of Al<sup>3</sup>. However, the fluorescence intensity is turned-on only in presence of  $\mathsf{AI}^{3+}$  ion with about 30 fold enhancements (Fig. S14b), the results showed that other metal ions do not interfere with the intensity of  $H_3L-AI^{3+}$  system and  $H_3L$  is specific for Al<sup>3+</sup> (Fig. S14c). Moreover, to understand the mode of complexation between H<sub>3</sub>L and Al<sup>3+</sup>, <sup>1</sup>H NMR titration have been performed in DMSO–D6 ( $H_3L$ ) and  $D_2O$  (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) solvents. On subsequent addition of Al3+ to H<sub>3</sub>L solution, the -OH peaks at 12.87, 10.87 and 9.36 ppm decrease and finally at 0.8 equiv. of Al<sup>3+</sup> all three –OH peaks completely disappear indicating the complex formation between H<sub>3</sub>L and Al3+ (Fig. S15). The stoichiometry of H<sub>3</sub>L–Al<sup>3+</sup> was confirmed by Job's method and mass spectrum which shows 1:2(M:L) complex formation (Fig. S16 and S17). Furthermore, reversibility of the chemosensor was also confirmed by the strong chelating agent ethylene-diamine-tetra-acetic acid (EDTA). The enhanced fluorescence intensity of H<sub>3</sub>L–Al<sup>3+</sup> was guenched after adding the EDTA, demonstrating the binding of  $H_3L$  with  $AI^{3+}$  is reversible in nature (Fig. 3b). The fluorescence quantum yield and average life time<sup>37</sup> of  $H_3L-Al^{3+}$  was observed to be  $\Phi =$ 0.182 and  $< \tau > = 3.60$  ns (Fig. S18 and Table S4). The performance comparison of H<sub>3</sub>L with other fluorescence sensor for Al<sup>3+</sup> is shown in Supplementary Table S5.



**Fig. 3** (a) Fluorescence spectra of  $H_3L$ , Inset: relative fluorescence intensity changes with respect to  $AI^{3+}$  concentration. (b) Fluorescence Spectra of  $H_3L$  (20  $\mu$ M) in the presence of 20 equiv. of  $AI^{3+}$  before and after treatment with excess EDTA ( $\lambda ex = 382$  nm).

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In summary, we successfully demonstrated an elastic crystal by introducing a new functionality such as azine group. The elastic nature of  $H_{3L}$  crystals was found to be consistent in MeOH, EtOH and ACN solvents by producing long to very long length crystals. Photo-irradiation on  $H_{3L}$  results in a SCSC phase transformation by twisting of the molecule along a axis. Moreover, the mechanistic pathway of SCSC transformation of  $H_{3L}$  to  $H_{3L}^{1}$  has been explained. These findings in solid-state crystalline materials could be of vital importance in the fields of crystal engineering and for the design of organic flexible materials, flexible electronics devices and optics. Further, due to excellent solubility, the solution state sensing behavior of  $H_{3L}$  was explored.  $H_{3L}$  displays highly selective, sensitive and reversible sensing behavior towards  $Al^{3+}$  with an LOD of 42 nM.

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# Notes and references

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- Q. Wei, K. Achazi, H. Liebe, A. Schulz, P.- L. M. Noeske, I. Grunwald and R. Haag, Angew. Chem. Int. Ed., 2014, 53, 11650.
- 2 Q. M. Zhang, H. Li, M. Poh, F. Xia, Z.Y. Cheng, H. Xu and C. Huang, *Nature* 2002, **419**, 284.
- A. L. Briseno, R. J. Tseng, M. M. Ling, E. H. L. Falcao, Y. Yang,
   F. Wudl and Z. Bao, *Adv. Mater.*, 2006, **18**, 2320.
- 4 Q. Tang, L. Li, Y. Song, Y. Liu, H. Li, W. Xu, Y. Liu, W. Hu and D. Zhu, Adv. Mater., 2007, 19, 2624.
- 5 E. C. W. Ou, L. Hu, G. C. R. Raymond, O. K. Soo, J. Pan, Z. Zheng, Y. Park, D. Hecht, G. Irvin, P. Drzaic and G. Gruner, ACS Nano 2009, 3, 2258.
- 6 J. A. Rogers, T. Someya and Y. Huang, *Science* 2010, **327**, 1603.
- 7 (a) M. Owczarek, K. A. Hujsak, D. P. Ferris, A. Prokofjevs, I. Majerz, P. Szklarz, H. Zhang, A. A. Sarjeant, C. L. Stern, R. Jakubas, S. Hong, V. P. Dravid and J. F. Stoddart, *Nat. Commun.*, 2016, 7, 13108; (b) L. Wen, L. Zhou, B. Zhang, X. Meng, H. Xu and D. Li, *J. Mater. Chem.*, 2012, 22, 22603.
- 8 G. R. Krishna, R. Devarapalli, G. Lal and C. M. Reddy, J. Am. Chem. Soc., 2016, **138**, 13561.
- 9 (a) S. Takamizawa and Y. Miyamoto, *Angew. Chem. Int. Ed.*, 2014, **53**, 6970; (b) S. Takamizawa and Y. Takasaki, *Angew. Chem. Int. Ed.*, 2015, **54**, 4815.
- 10 S. Saha and G. R. Desiraju, Chem. Commun., 2016, 52, 7676.
- 11 P. Fratzl and F. G. Barth, *Nature* 2009, **462**, 442.
- 12 Y. Cao and H. Li, Nat. Nanotechnol., 2008, 3, 512.
- 13 (a) M. K. Panda, S. Ghosh, N. Yasuda, T. Moriwaki, G. D. Mukherjee, C. M. Reddy and P. Naumov, *Nat. Chem.*, 2015, **7**, 65; (b) L. Pejov, M. K. Panda, T. Moriwaki and P. Naumov, *J. Am. Chem. Soc.*, 2017, **139**, 2318; (c) D. P. Karothu, J. Weston, I. T. Desta and P. Naumov, *J. Am. Chem. Soc.*, 2016, **138**, 13298.
- 14 C. M. Reddy, M. T. Kirchner, R. C. Gundakaram, K. A. Padmanabhan and G. R. Desiraju, *Chem.–Eur. J.*, 2006, **12**, 2222.
- 15 S. Saha and G. R. Desiraju, J. Am. Chem. Soc., 2017, **139**, 1975.

- S. Ghosh, M. K. Mishra, S. B. Kadambi, U. Ramamurty and G. R. Desiraju, Angew. Chem. Int. Ed., 2015, 54, 2634 C7CC04392A
- 17 A. C. Maahs, M. G. Ignacio, M. Ghazzali, D. V. Soldatov and K. E. Preuss, *Cryst. Growth Des.*, 2017, **17**, 1390.
- 18 O. S. Bushuyev, T. C. Corkery, C. J. Barrett and T. Friscic, *Chem. Sci.*, 2014, 5, 3158.
- (a) N. L. Toh, M. Nagarathinam and J. J. Vittal, Angew. Chem. Int. Ed., 2005, 44, 2237; (c) G. Liu, J. Liu, Y. Liu and X. Tao, J. Am. Chem. Soc., 2014, 136, 590.
- 20 (a) H. Aggarwal, P. M. Bhatt, C. X. Bezuidenhout and L. J. Barbour, *J. Am. Chem. Soc.*, 2014, **136**, 3776; (b) J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart and O. M. Yaghi, *Chem. Sci.*, 2013, *4*, 2858; (c) S. Shin, S. Jeong, D. Kim and M. S. Lah, *Cryst. Growth Des.*, 2017, *17*, 2228.
- 21 (a) M. A. Sinnwell and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2016, **55**, 3477; (b) M. H. Mir, L. L. Koh, G. K. Tan and J. J. Vittal, *Angew. Chem. Int. Ed.*, 2010, **122**, 400; (c) G. S. Papaefstathiou, Z. Zhong, L. Geng and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2014, **126**, 9158.
- 22 T. Kim, L. Zhu, L. J. Mueller and C. J. Bardeen, J. Am. Chem. Soc., 2014, **136**, 6617.
- 23 (a) Y. Wang and N. Herron, *J. Phys. Chem.*, 1991, 95, 525; (b)
  M. Bendikov and F. Wudl, *Chem. Rev.*, 2004, 104, 4891; (c) P. K. Jain, X. Huang, I. H. El-Sayed, M, El-Sayed, *Acc. Chem. Res.*, 2008, 41, 1578; (d) S. Lv, D. M. Dudek, Y. Cao, M. M. Balamurali, J. Gosline and H. Li, *Nature* 2010, 465, 69.
- 24 Y. Hong, J. W. Y. Lam and B. Z. Tang, Chem. Soc. Rev., 2011, 40, 5361.
- 25 W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159.
- 26 K. P. Carter, A. M. Young and A. E. Palmer, *Chem. Rev.*, 2014, 114, 4564.
- 27 S. Ghosh and C. M. Reddy, Angew. Chem. Int. Ed., 2012, 51, 10319.
- (a) D. B. Brown and M. Fatemi, J. Appl. Phys., 1980, 51, 2540;
  (b) D. L. Dorset, Acta. Cryst. A., 1980, 36, 592.
- (a) B. I. Yakobson, C. J. Brabec and J. Bernholc, *Phys. Rev. Lett.*, 1996, **76**, 2511; (b) R. Martel, H. R. Saha and P. Avouris, *J. Phys. Chem. B.*, 1999, **103**, 7551.
- 30 D. J. Barber and R. London, An Introduction to the Properties of Condensed Matter, Cambridge University Press, Cambridge, 1989.
- 31 (a) V. A. Atrazhev, S. F. Burlatsky, D. V. Dmitriev and V. I. Sultanov, J. Stat. Mech., 2013, **13**, 2004; (b) S. M. Notley, B. Pettersson and L. Wagberg, J. Am. Chem. Soc., 2004, **126**, 13930.
- 32 O. S. Bushuyev, A. Tomberg, T. Frisčič and C. J. Barrett, J. Am. Chem. Soc., 2013, 135, 12556.
- 33 S. Jacimovski and D. Rakovic, Acta Phys. Pol. Acta., 2011, 120, 231.
- 34 A. K. Saini, V. Sharma, P. Mathur and M. M. Shaikh, Sci. Rep., 2016, 6, 34807.
- 35 S. Kim, J. Y. Noh, K. Y. Kim, J. H. Kim, H. K. Kang, S.-W. Nam, S. H. Kim, S. Park, C. Kim and J. Kim, *Inorg. Chem.*, 2012, **51**, 3597.
- 36 Y. Lu, S. Huang, Y. Liu, S. He, L. Zhao and X. Zeng, *Org. Lett.*, 2011, **13**, 5274.
- 37 E. Heyer, P. Lory, J. Leprince, M. Moreau, A. Romieu, M. Guardigli, A. Roda and R. Ziessel, *Angew. Chem. Int. Ed.*, 2015, 54, 2995.

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Multifunctional azine ligand with elastic bending with full phase retention, photoinduced SCSC transformation and sensitive Al<sup>3+</sup> detection