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Palladium-induced transformation of nematic liquid crystals to robust metallogel comprising self-assembled nanowires[†]

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The formation of a nematic liquid-crystalline phase in the bulk along with gelation of a novel asymmetric bolaamphiphilic NDI scaffold has been demonstrated. Further, a discrete metal NDI complex that is capable of forming a robust metallogel through wrapping of the NDI core with the oxyethylene chains of the neighboring molecules has been synthesized.

Nature has shown astonishing capabilities of creating complex supramolecular assemblies through weak inter-molecular interactions that are capable of pursuing highly specific functions. Inspired by nature, chemists have utilized such non-covalent interactions as a tool to engineer complex supramolecules including liquid crystals (LCs) and gelators. Self-assembled molecules with long-range orientational order often show liquid crystalline properties.¹ In thermotropic LCs, long-range order could be achieved by slowly cooling from the isotropic melt.² However, if the long-range order is reached by dissolving the molecules in a solvent above a particular concentration, they are called lyotropic LCs.3 Such long-range orientational order in these materials could be utilized in the construction of molecular ferroic and LC memory devices.⁴ On the other hand, the self-assembly of molecules in a specific solvent could also form supramolecular gels which have received extensive attention owing to their potential utilization in multiple areas.⁵

Since metal-ligand bond formation is as facile as the other non-covalent interactions, such interactions could be used to fabricate complex superstructures, especially metallogels that can adopt smart functionalities similar to natural supramolecules.⁶ In general, two strategies could be exploited to design supramolecular metallogels: (i) *in situ* metal–ligand coordination driven formation of supramolecular polymers which eventually transform into metallogels in certain solvents or (ii) construction of a discrete metal–ligand low molecular mass complex as a monomeric unit for the fabrication of supramolecular polymeric metallogels *via* multiple non-covalent interactions. The emerging area of metallogels has witnessed fascinating advancements in molecular recognition, *in situ* syntheses of metal nanoparticles, catalysis, applications in magnetic resonance imaging, dispersion of carbon-based nanomaterials, and so on.⁷ Inorganic–organic hybrid complexes are also potential candidates for developing multiferroic materials.⁸ In spite of the existence of a large body of data on metallogels, there is continuous interest in the design of novel metallogels to solve hitherto unexplored issues.

Naphthalenediimides (NDIs) are among the most promising n-type organic semiconductors, which hold strong interest in areas as diverse as solar cells, photovoltaic devices, light harvesting systems, organic field effect transistors, liquid crystal displays, *etc.*⁹ On the other hand, NDI based self-assemblies possessing compelling nano-structures such as fibers, belts, ribbons, solid spheres, and vesicles have been studied extensively in the last two decades to explore various possibilities.¹⁰ Although there have been several reports on NDI based supramolecular gels, metallogels comprising the NDI moiety are rare.¹¹ Herein, we report design, synthesis, and characterization of a NDI based nematic liquid crystalline ligand which forms a discrete metalligand complex amenable to self-organization into a robust metallogel.

The synthesis of an asymmetric bolaamphiphilic NDI derivative, **1**, a waxy solid, is given in Scheme 1 and also in the ESI.[†] Differential scanning calorimetry (DSC) of **1** in the bulk displayed a weak endothermic transition at ~136.6 °C followed by melting at ~147.7 °C, suggesting the probable existence of a narrow LC phase in between these two temperatures (Fig. S1, ESI[†]). During cooling from its isotropic melt state, a broad exotherm appeared at ~116.8 °C. Under a polarized optical microscope (POM), a weakly birefringent LC phase appeared after 130 °C during



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Scheme 1 Schematic illustrations of the synthesis of an asymmetric bolaamphiphilic NDI derivative, **1**, and its discrete metal complex **2**.

heating (Fig. S2, ESI[†]). The birefringence vanished above 140 $^{\circ}$ C, which is in line with the observed DSC data. During cooling from the isotropic melt, a highly birefringent LC phase appeared at around 130 $^{\circ}$ C (Fig. 1a and Fig. S3, ESI[†]). It is important to note that the corresponding transition was not observed in the DSC thermogram, indicating the probable nematic nature of the LC phase.¹² A LC to crystalline phase transition was observed at around 120 $^{\circ}$ C, which is in accord with the DSC data (Fig. 1a and Fig. S2 and S3, ESI[†]).

Finally, variable temperature X-ray diffraction (XRD) studies revealed that **1** in the bulk persisted in the crystalline state up to ~130 °C. The LC phase appeared above 130 °C and finally melted at ~150 °C as indicated by the absence of any XRD signal at that temperature (Fig. 1b). The emergence of the firstorder reflection peak at ~2.6 nm ($2\theta = 3.4^{\circ}$), which is relatively smaller than the estimated molecular length of **1**, and a broad peak in the wide-angle regime confirmed the presence of a nematic LC phase (Fig. S4, ESI†).^{12b} Similarly, XRD pattern characteristics of the nematic phase also appeared during cooling from the isotropic melt state before transforming into the crystalline state, thus confirming the enantiotropic nature of the LC phase.^{12b}

The propensity of **1** to undergo self-aggregation in the solution state was checked after investigating its self-assembly in the bulk. A hot solution of **1** in EtOH was transformed into a robust gel upon spontaneous cooling beyond a critical gelation concentration (CGC) of 10.4 mM. A similar gelation propensity, however, was not observed in other organic solvents like methanol, DCM, THF, acetonitrile, methylcyclohexane, benzene, toluene and water



Fig. 2 (a) Phase-contrast optical microscopy image of 1 (gel) from EtOH. The inset in panel a shows the photograph of the gel of 1 in EtOH. (b) Powder XRD pattern of the freeze-dried gel of 1 from EtOH.

(Table S1, ESI[†]). The critical aggregation concentration (CAC) in EtOH measured from the concentration-dependent UV-Vis spectra was around 1.2 mM (Fig. S5a and b, ESI⁺). Morphological studies revealed the formation of fibrous networks with a length in the range of several micrometers (Fig. 2a and Fig. S6, ESI[†]). Powder X-ray diffraction (PXRD) studies of the freezedried gel of 1 revealed the appearance of a strong first-order Bragg reflection peak at $2\theta = 2.92^{\circ}$ (~3 nm) along with the repetitive reflections up to the sixth order (Fig. 2b). This result indicates the existence of a highly ordered lamellar organization of **1** with a π - π stacking distance of 0.38 nm in EtOH (Fig. 2b). The layered distance of ~ 3 nm in the lamellae matched well with the estimated molecular length of 1 (\sim 3 nm, Fig. S4, ESI⁺), indicating the formation of a 'monolayer' assembly.¹³ Moreover, the hydrazide units, which are located only on one side of the bolaamphiphilic 1, have a strong tendency to form orthogonal H-bonds among themselves. Parallel alignment of 1 in the monolayer of the lamellae also allows the H-bonded hydrazide units to stay on the same side. Based on these observations, a probable molecular packing of 1 in the aggregates in EtOH is proposed (Fig. S7, ESI[†]).

Since the pyridyl units are prone to form a coordination complex with various metal ions, we further attempted to synthesize a discrete metal complex of **1** by reacting it with $PdCl_2(PhCN)_2$ in a 2:1 molar ratio in dichloromethane (DCM). To our surprise, we observed transformation of the above mixture into a stable, light yellow colored gel in DCM after completion of the reaction (Fig. 3a inset, CGC, [2] = 3.8 mM). Thin layer chromatographic (TLC) as well as ¹H-NMR investigations



Fig. 1 (a) Photograph of the nematic LC phase appeared during cooling from the isotropic melt of **1** (in the bulk) under a POM. (b) Variable temperature XRD studies of **1** (in the bulk).



Fig. 3 (a) Gradual evolution of metallogel 2 in DCM upon aging probed by a transmittance method. The inset in panel a shows the photograph of the metallogel 2 in DCM. (b) AFM image of the metallogel 2 ([2] = 0.3 mM) from DCM.

confirmed the quantitative formation of the discrete metal complex/ gel (2) (Fig. S8, ESI⁺). A similar gelation propensity was also observed in CHCl₃ (Table S2, ESI[†]). The kinetics of gel formation was found to depend strongly on the concentration of the $2:1 \text{ 1/PdCl}_2(\text{PhCN})_2$ complex as well as on the nature of the solvent. The rate of gel formation was faster in DCM than that in CHCl₃. Since the gel of 2 is translucent in appearance, we probed the kinetics of gelation via a transmittance method. Interestingly, the transmittance of the mixture in DCM started to decrease after ~ 10 min and got saturated after 30 min, showing the maximum rate in between (Fig. 3a). UV/ Vis spectroscopic studies at variable concentrations revealed that the relative intensity of the absorption bands arising from the NDI core at 358 and 378 nm reversed in intensity upon increasing the concentration beyond 0.2 mM, indicating the onset of aggregation (Fig. S9a and b, ESI⁺). Morphological studies revealed the presence of entangled nanowires with high aspect ratios which constituted the metallogel (Fig. 3b and Fig. S9c, d, ESI⁺).

Rotating-frame Overhauser effect (ROESY) NMR spectroscopic studies of the metallogel in $CDCl_3$ were performed in order to find probable molecular packing among the gelators, which revealed the presence of multiple through-space coupling signals among the protons (H_a and H_b) of the NDI core and the protons (H_i, H_j and H_k) of the oxyethylene chains attached to the NDI core of the adjacent molecule of **2** (Fig. 4b and Fig. S10, ESI[†]). Multiple through-space coupling signals among the proton (H_f) of the hydrazide unit and most of the protons of the oxyethylene chains indicate the existence of hydrogen-bonding interactions among the hydrazide unit and oxygen atoms of the oxyethylene chains in the self-assembled networks. These results strongly indicate that the NDI moieties in one of the discrete complex of **2** lie in close proximity with the oxyethylene chains that belong to the adjacent metal complex of **2**. This structural organization in 3D was further corroborated by the existence of through-space coupling signals between the protons of the oxyethylene chains of **2** and the protons of the gallate unit (H_e) belonging to the adjacent molecule of **2**.

In addition, powder XRD patterns of the freeze-dried gel of 2 from DCM showed the appearance of three broad Bragg reflections, indicating low crystallinity of the dried gel (Fig. 4a). The corresponding *d*-spacings of these peaks were 1.48, 0.72 and 0.51 nm with an approximate ratio of 1:1/2:1/3, suggesting lamellar packing of the gelators. However, a layered thickness of ~1.5 nm of the lamellae obtained from the XRD pattern was much smaller relative to the estimated molecular length of 2 (~5.7 nm, Fig. S11, ESI†),



Fig. 4 (a) Powder XRD pattern of the dried gel of 2 from DCM. (b) Selected areas in the ROESY NMR spectrum (CDCl₃, 700 MHz, 10 mM, 293 K) of the gel of 2. Cross-peak signals inside the red boxes are due to through space coupling. (c) A graphical representation of the molecular packing of 2 in the metallogel matrix based on ROESY and XRD data.

which suggests that the oxyethylene chains of one molecule presumably wrap around the NDI core of the adjacent molecule of 2 (Fig. 4c). The bending of the oxyethylene chains during the wrapping may eventually reduce the effective length of 2. Further, tilting of the molecular alignment in the lamellae may account for the observed layered thickness in the gel. Therefore the conclusion drawn from the ROESY NMR experiment was further verified by XRD studies. On the other hand, unlike 1 in the bulk, complex 2 did not display any LC behavior as it decomposed upon heating at ~ 220 °C under a POM (Fig. S12, ESI[†]).

In summary, we demonstrated the synthesis of a novel asymmetric bolaamphiphilic NDI derivative, 1, capable of showing a thermotropic nematic LC phase in the bulk. 1 also formed a stable gel in EtOH. Further, we synthesized a novel metal-ligand discrete complex (2) in nearly quantitative yield by reacting an equimolar amount of 1 and PdCl₂(PhCN)₂. Complex 2 was found to yield a stable gel in DCM or in CHCl₃ through the formation of nanowires of high aspect ratio. The formation of relatively high aspect ratio fibers/nanowires by the metallogelators relative to the low aspect ratio fibers of 1 (although in a different solvent) clearly explained the lower CGC value of the metallogel (CGC: 3.8 mM) compared to the gel of 1 (CGC: 10.4 mM). Therefore, the discrete metal complex of 1 showed an enhanced ability to self-assemble compared with the molecule of 1 alone. Further studies including the preparation of NDI based metallogels in aqueous medium with nascent potential are underway.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) C. Tschierske, Chem. Soc. Rev., 2007, 36, 1930; (b) T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann and S. Laschat, Chem. Rev., 2016, 116, 1139; (c) T. Kato, Y. Hirai, S. Nakaso and M. Moriyama, Chem. Soc. Rev., 2007, 36, 1857.
- 2 (a) J. W. Goodby, V. Görtz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegnu, P. Boullanger, D. Lafont, Y. Queneau, S. Chamberte and J. Fitremann, *Chem. Soc. Rev.*, 2007, 36, 1971; (b) X. Qiao, P. Sun, A. Wu, N. Sun, B. Dong and L. Zheng, *Langmuir*, 2019, 35, 1598; (c) S. Datta and S. Bhattacharya, *Soft Matter*, 2015, 11, 1945.
- 3 (*a*) L. van 't Hag, S. L. Gras, C. E. Conn and C. J. Drummond, *Chem. Soc. Rev.*, 2017, **46**, 2705; (*b*) J. Zhai, N. Tran, S. Sarkar, C. Fong, X. Mule and C. J. Drummond, *Langmuir*, 2017, **33**, 2571; (*c*) Y. Huang and S. Gui, *RSC Adv.*, 2018, **8**, 6978.
- 4 (a) A. S. Tayi, A. Kaeser, M. Matsumoto, T. Aida and S. I. Stupp, *Nat. Chem.*, 2015, 7, 281; (b) K. Takae and H. Tanaka, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, 115, 9917; (c) F. Serra, M. Buscaglia and T. Bellini, *Mater. Today*, 2011, 14, 488; (d) P. Heremans, G. H. Gelinck, R. Muller, K.-J. Baeg, D.-Y. Kim and Y.-Y. Noh, *Chem. Mater.*, 2011, 23, 341.

- R. G. Weiss, J. Am. Chem. Soc., 2014, 136, 7519; (b) A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, Angew. Chem., Int. Ed., 2008, 47, 8002; (c) K. Maeda, H. Mochizuki, K. Osato and E. Yashima, Macromolecules, 2011, 44, 3217; (d) T. Aida, E. W. Meijer and S. I. Stupp, Science, 2012, 335, 813; (e) M. Fleischer and C. Schmuck, Chem. Commun., 2014, 50, 10464; (f) Q. Liu, M. Zhao, S. Mytnyk, B. Klemm, K. Zhang, Y. Wang, D. Yan, E. Mendes and J. H. van Esch, Angew. Chem., Int. Ed., 2019, 58, 547; (g) S. Bhattacharjee and S. Bhattacharya, J. Mater. Chem. A, 2014, 2, 17889; (h) D. Bhagat, S. K. Samanta and S. Bhattacharya, ACS Appl. Mater. Interfaces, 2013, 5, 8394; (j) S. K. Samanta, K. S. Subrahmanyam, S. Bhattacharya and C. N. R. Rao, Chem. – Eur. J., 2012, 18, 2890.
- 6 (a) B. Xing, M. F. Choi, Z. Zhou and B. Xu, Langmuir, 2002, 18, 9654;
 (b) M. J. Mayoral, C. Rest, V. Stepanenko, J. Schellheimer, R. Q. Albuquerque and G. Fernández, J. Am. Chem. Soc., 2013, 135, 2148;
 (c) C. Rest, M. J. Mayoral, K. Fucke, J. Schellheimer, V. Stepanenko and G. Fernández, Angew. Chem., Int. Ed., 2014, 53, 700; (d) Y. Liu, T. Wang, Z. Li and M. Liu, Chem. Commun., 2013, 49, 4767;
 (e) E. Noh, S. Park, S. Kang, J. Y. Lee and J. H. Jung, Chem. Eur. J., 2013, 19, 2620; (f) S. Bhowmik, B. N. Ghosh, V. Marjomäki and K. Rissanen, J. Am. Chem. Soc., 2014, 136, 5543; (g) B. N. Ghosh, S. Bhowmik, P. Mal and K. Rissanen, Chem. Commun., 2014, 50, 734;
 (h) Y. He, Z. Bian, C. Kang and L. Gao, Chem. Commun., 2011, 47, 1589; (i) J. M. J. Paulusse, D. J. M. van Beek and R. P. Sijbesma, J. Am. Schem. Soc., 2007, 129, 2392; (j) B. Maiti, S. Bhattacharjae and S. Bhattacharya, Nanoscale, 2019, 11, 2223; (k) S. Bhattacharjee and S. Bhattacharya, Chem. Commun., 2014, 50, 11690.
- 7 (a) M. O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960; (b) A. Y. Tam and V. W. Yam, *Chem. Soc. Rev.*, 2013, **42**, 1540; (c) J. H. Jung, J. H. Lee, J. R. Silverman and G. John, *Chem. Soc. Rev.*, 2013, **42**, 924; (d) P. K. Vemula, U. Aslam, V. A. Mallia and G. John, *Chem. Mater.*, 2007, **19**(2), 138; (e) N. Malviya, C. Sonkar, B. K. Kundu and S. Mukhopadhyay, *Langmuir*, 2018, **34**, 11575; (f) J. Huang, L. He, J. Zhang, L. Chen and C.-Y. Su, *J. Mol. Catal. A: Chem.*, 2010, **317**, 97; (g) S. R. Bull, M. O. Guler, R. E. Bras, T. J. Meade and S. I. Stupp, *Nano Lett.*, 2005, **5**, 1.
- 8 (a) M. M. Abdelkader and M. Abdelmohsen, *Mater. Res. Express*, 2018, 6, 025608; (b) L. Xin, Z. Zhang, M. A. Carpenter, M. Zhang, F. Jin, Q. Zhang, X. Wang, W. Tang and X. Lou, *Adv. Funct. Mater.*, 2018, 28, 1806013; (c) Y. Zhang, W.-Q. Liao, D.-W. Fu, H.-Y. Ye, C.-M. Liu, Z.-N. Chen and R.-G. Xiong, *Adv. Mater.*, 2015, 27, 3942; (d) B. Huang, L.-Y. Sun, S.-S. Wang, J.-Y. Zhang, C.-M. Ji, J.-H. Luo, W.-X. Zhang and X.-M. Chen, *Chem. Commun.*, 2017, 53, 5764.
- 9 (a) S. V. Bhosale, C. H. Jani and S. J. Langford, *Chem. Soc. Rev.*, 2008, 37, 331; (b) F. Würthner and M. Stolte, *Chem. Commun.*, 2011, 47, 5109; (c) T. He, M. Stolte and F. Würthner, *Adv. Mater.*, 2013, 25, 6951; (d) N. Sakai, J. Mareda, E. Vauthey and S. Matile, *Chem. Commun.*, 2010, 46, 4225; (e) M. A. Kobaisi, S. V. Bhosale, K. Latham, M. A. Raynor and S. V. Bhosale, *Chem. Rev.*, 2016, 116, 11685; (f) N. V. Ghule, R. S. Bhosale, S. V. Bhosale, T. Srikanth, N. V. S. Rao and S. V. Bhosale, *ChemistryOpen*, 2018, 7, 61.
- 10 (a) S. Basak, J. Nanda and A. Banerjee, *Chem. Commun.*, 2013, 49, 6891; (b) K. Liu, C. Wang, Z. B. Li and X. Zhang, *Angew. Chem., Int. Ed.*, 2011, 50, 4952; (c) H. Shao, T. Nguyen, N. C. Romano, D. A. Modarelli and J. R. Parquette, *J. Am. Chem. Soc.*, 2009, 131, 16374; (d) H. Shao and J. R. Parquette, *Chem. Commun.*, 2010, 46, 4285; (e) M. Kumar and S. J. George, *Nanoscale*, 2011, 3, 2130; (f) A. Das and S. Ghosh, *Chem. Commun.*, 2016, 52, 6860.
- 11 S. Ganta and D. K. Chand, Inorg. Chem., 2018, 57, 3634.
- 12 (a) B. V. Roie, J. Leys, K. Denolf, C. Glorieux, G. Pitsi and J. Thoen, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, 72, 041702; (b) S. Bhattacharjee, S. K. Samanta, P. Moitra, K. Pramoda, R. Kumar, S. Bhattacharya and C. N. R. Rao, *Chem. – Eur. J.*, 2015, 21, 5467.
- 13 (a) S. Bhattacharjee and S. Bhattacharya, Chem. Asian J., 2015, 10, 572; (b) A. Sikder, A. Das and S. Ghosh, Angew. Chem., Int. Ed., 2015, 54, 6755.