CrystEngComm

Cite this: *CrystEngComm*, 2011, **13**, 6706

www.rsc.org/crystengcomm

PAPER

Supramolecular luminescent system based on 2-cyano-3(4-(diphenylamino) phenyl) acrylic acid: Chiral luminescent host for selective CH_3CN sensor†

Savarimuthu Philip Anthony,[ab] Colm Delaney,[a] Sunil Varughese,[a] Longsheng Wang[a] and Sylvia M. Draper*[a]

Received 9th February 2011, Accepted 11th August 2011
DOI: 10.1039/c1ce05187c

New supramolecular luminescent host systems based on 2-cyano-3(4-(diphenylamino)phenyl) acrylic acid (CDPA), a triphenylamine based luminescent acid, and amines (propylamine (**1**), dimethylaminopyridine, DMAP (**2**) and (1*S*,2*R*)-2-amino-1,2-diphenylethanol (**3**)) were prepared using a supramolecular approach. For each, the inclusion of amines in the CDPA matrix led to blue shifts in the solid state luminescence. **1** forms a CH_3CN-selective, luminescent host and exhibits solvent dependent luminescent changes in the solid state. Crystallisation of CDPA-DMAP from EtOAc (**2a**) and CH_3CN (**2b**) produces two different solid forms which exhibit slight differences in luminescence (λ_{max} at 522 nm and 529 nm, respectively). The chiral luminescent host system (**3a**) obtained from CH_3CN shows robust, reversible CH_3CN-selective luminescent sensing (λ_{max} at 523 nm (with CH_3CN) and 553 nm (without CH_3CN)). In this case the luminescence changes with the crystallising solvent (MeOH (**3b**) and EtOH (**3c**)).

Introduction

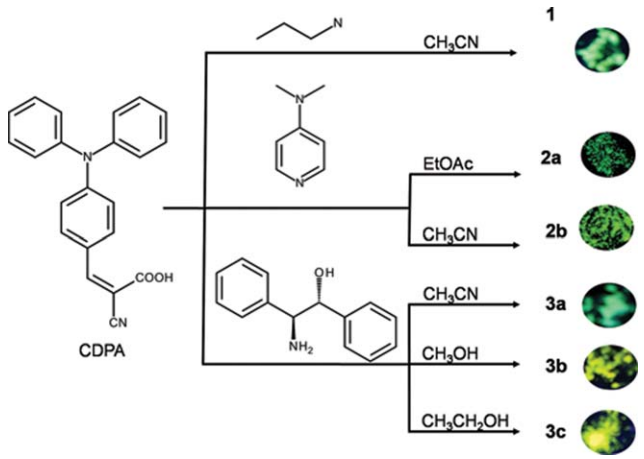
Luminescent materials find application in fields from environmental monitoring to biomedical diagnostics, because of their high sensitivity.[1] Hence several efficient organic luminophores with strong luminescence in solution have been developed for use in pH, metal ion and anion sensing, and bio-imaging.[2] However, the development of functional materials based on solid-state organic luminescence is rare due to quenching by molecular aggregation or strong H-bonding.[3] The potential application of solid-state luminescent materials in organic electroluminescence (EL), optoelectronic devices and sensors, accounts for recent interest in this area.[4] Chiral luminescent materials, in particular, can exhibit circularly polarized luminescence (CPL).[5] Porous or host–guest luminescent organic materials, are interesting candidates in analytical chemistry because of their guest dependent optical properties which can be exploited for sensor applications.[6,7] The unpredictable nature of the formation of such luminescent, porous or host–guest structures has limited their development in robust sensor applications.

Supramolecular luminescent systems composed of two or more organic components are desirable from a synthetic viewpoint, although the prediction of the supramolecular structure is difficult as it often results in host structures with included solvent molecules.[8–13] Nevertheless, the supramolecular approach offers a wealth of opportunity for simple variation (by changing one of the co-crystallisation components) and excellent scope for tuning the solid-state luminescence by control of the solid-state structure.[12] Despite its simplicity a supramolecular approach has not been widely used in generating porous or host–guest luminescent systems. An exception is the work of Imai *et al.* where they report supramolecular luminescent host systems derived from mixing luminescent organic acids and amines and demonstrate their solvent-dependent, solid-state optical properties.[9,10,12] Recently we reported the switching and tuning of organic solid-state luminescence in 2-cyano-3(4-(diphenylamino) phenyl) acrylic acid (CDPA) by forming unusual intermolecular H-bond interactions with amines.[11] The unusual intermolecular interactions of amines (pyridine, piperidine, pyrrolidine and morpholine) with CDPA leads to the gradual blue shift of CDPA solid state luminescence from 587 nm to 496 nm and the crystalline host system of CDPA-piperidine displays selective CH_3CN luminescence switching. This unusual attribute of CDPA prompted us to investigate the formation of supramolecular luminescent host systems of CDPA with chiral amines. Changes in the fluorescence of such systems, on interacting with chiral guests, can provide time-efficient and sensitive enantiomer determination of chiral reagents *e.g.* catalysts, natural products and drugs.[14]

In this manuscript, we report supramolecular luminescent hosts generated from CDPA and amines, which exhibit selective CH_3CN-dependent, solid-state luminescence (Scheme 1). Co-crystallisation of CDPA with propylamine produces a luminescent host system **(1)** with included CH_3CN solvent molecules in

[a]*School of Chemistry, Trinity College Dublin, Dublin 2, Ireland. E-mail: smdraper@tcd.ie; Fax: +353 16712826; Tel: +353 18962026*
[b]*Present address: School of Chemical & Biotechnology, SASTRA University, Thanjavur-613401 Tamil Nadu, India*

† Electronic supplementary information (ESI) available: Alternative representation of crystal packing in **1**, TGA for **1**, **2a/2b** and **3**, Circular dichroism spectrum of **3a**, Comparison of solid state luminescent intensity of CDPA, **1**, **2a** and **3a**. CCDC reference numbers 797566 and 797567. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05187c



Scheme 1 CDPA-amine supramolecular luminescent systems.

the crystal lattice. The chiral supramolecular system prepared from CDPA and the chiral amine (1*S*,2*R*)-2-amino-1,2-diphenylethanol **(3a)** exhibits robust CH_3CN-dependent luminescent sensing as well as luminescent properties that differ depending on the crystallising solvent. Co-crystallization of CDPA with dimethylaminopyridine (DMAP) produces two different solid forms **(2a, 2b)** for which the solid-state luminescence changes with the crystallising solvent.

Experimental

Synthesis and characterization

Triphenylamine, cyanoacetic acid, $POCl_3$, anhydrous dimethyl formamide (99.8%), propylamine, dimethylaminopyridine, and (1*S*,2*R*)-2-amino-1,2-diphenylethanol were obtained from Aldrich and used as received. Elemental analyses were measured with a Perkin-Elmer 2400 II CHN analyzer. Thermogravimetric analyses (TGA) were carried out using a Perkin Elmer Pyris-1 TGA under both nitrogen and oxygen flow using a platinum crucible (*ca.* 5 mg sample; heating rate of 10 °C min^{-1}; range 25–900 °C). The instrument was calibrated to In and Ni standards in air atmosphere. Co-crystallisations were performed in air under ambient conditions, using HPLC grade solvents.

2-cyano-3(4-(diphenylamino)phenyl)acrylic acid (CDPA). A 70 mL acetonitrile solution of 4-diphenylaminobenzaldehyde (1.0 g, 3.66 mmol), cyanoacetic acid (0.34 g, 4.0 mmol), and piperidine (0.62 g, 7.32 mmol) was refluxed for 4 h under a nitrogen atmosphere. Solvent removal by rotary evaporator followed by solvent extraction (CH_2Cl_2 and *aq.* HCl (0.1 M)) yielded the product as a dark purple solid, (1.05 g, 85%): Mp 213-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.90 (d, 2H), 7.39 (t, 4H), 7.23 (m, 6H), 6.98 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 155.0, 153.2, 145.1, 132.7, 129.6, 126.3, 125.5, 122.8, 118.2, 116.9, 95.5.

1: A mixture of CDPA (100 mg, 0.29 mmol) and propylamine (0.3 mmol) was dissolved in acetonitrile (15 ml) and left to stand at room temperature. Crystalline needles of **1** form after 4–5 h in 90% yield. $C_{25}H_{25}N_3O_2$ (399.48): calcd. C 75.16, H 6.31, N 10.52; found C 74.95, H 6.34, N 10.42.

2: A mixture of CDPA (100 mg, 0.29 mmol) and dimethylaminopyridine (0.3 mmol) was dissolved in acetonitrile (15 mL) or ethyl acetate (15 mL) as two separate experiments. Acetonitrile solutions produced crystalline flakes of **2b** on standing at room temperature for 12 h. $C_{29}H_{26}N_4O_2$ (462.54): calcd. C 75.30, H 5.67, N 12.11; found C 75.15, H 5.64, N 11.99. Ethyl acetate gave an 85% yield of single crystals of **2a** after 8 h. $C_{29}H_{26}N_4O_2$ (462.54): calcd. C 75.30, H 5.67, N 12.11; found C 75.06, H 5.58, N 11.99.

3: A mixture of CDPA (100 mg, 0.29 mmol) and (1*S*,2*R*)-2-amino-1,2-diphenylethanol (0.3 mmol) was dissolved in acetonitrile (15 mL), methanol (15 mL) and ethanol (20 mL) as three separate reactions. Acetonitrile and methanol solutions produce crystalline fibres of **3a** and **3b** respectively within 1 day. Ethanol solutions gave crystalline thin plates (**3c**) after standing at room temperature for one week. In all three solvents the crystalline product yield was 85%. $C_{36}H_{31}N_3O_3 \cdot H_2O$ (571.65). calcd. C 75.64, H 5.82, N 7.35; found in **3a**, C 75.77, H 5.50, N 7.18; **3b**, C 75.35, H 5.78, N 7.25; **3c**, C 75.22, H 5.76, N 7.23.

Details of UV-visible, circular dichroism and luminescence studies

Absorption and luminescence spectra were recorded using a Perkin Elmer Lambda 1050 and Horiba Jobin Yvon Fluorolog instrument. Solid state luminescence was measured by spreading the powdered samples on a glass plate. To compare the intensity of the solid state luminescence with CDPA in CH_2Cl_2 solution, transparent KBr pellets of CDPA, **1–3** were prepared and the concentration of the compounds in solution as well as in the solid matrix were adjusted to keep the optical density (OD) around 0.5. KBr pellets of these samples show similar luminescence λ_{max} as their pure solid samples. Circular dichroism studies used a Jasco J-810 Spectropolarimeter.

Details of powder X-ray diffraction (PXRD) and single crystal studies

PXRD measurements were recorded using a Siemens diffractometer-D500 at room temperature.

Single crystals were immersed in oil and carefully chosen after they were viewed through a polarizing microscope. The crystals were glued to a thin glass fibre using an adhesive (cyano acrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The data collection was carried out at 150 K and the crystals were smeared in NIH immersion oil to protect them from ambient laboratory conditions. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS.[15] The structure solution of all the complexes was carried out by direct methods, and refinements were performed by full-matrix least-squares on F^2 using the SHELXTL-PLUS[16] suite of programs. All the structures converged to good *R* factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed on calculated positions using appropriate HFIX options in SHELXTL and were refined isotropically. Intermolecular interactions were computed using the PLATON program.[17]

Results and discussion

Organic luminescent acid, CDPA, a triphenylamine derivative, was synthesized following the literature procedure.[18] CDPA

exhibits strong luminescence in CH_2Cl_2 solutions with λ_{max} at 603 nm and estimated quantum yield (Φ_f) 0.165 (on comparison with coumarin 6). Solid CDPA luminesces with similar intensity.[11] Supramolecular luminescent organic systems were prepared by crystallising CDPA with different amines in CH_3CN, EtOAc and alcohol (Scheme 1). The crystalline product of **1** could be obtained from CH_3CN solvent only. Ethyl acetate, methanol, ethanol, methylene chloride and toluene were the other solvents tested for the preparation of CDPA supramolecular luminescent systems.

Single crystal X-ray diffraction data provided insight into the structural organization and guest-inclusion processes of these supramolecular luminescent solids. The crystal lattice of CDPA exhibits a helical network generated *via* O–H···NC interactions involving the carboxyl and cyano groups.[11] In **1**, the amine deprotonates CDPA to form ionic N^+–H···O^- interactions in the crystal lattice (Fig. 1a, Table 1). The $-NH_3^+$ interacts with three different CDPA molecules, forming a one-dimensional network structure along the *b*-axis. In addition, lateral molecules are stabilized by weak C–H···π interactions. The guest CH_3CN molecules are included in the space created between two adjacent one-dimensional chains however they are not involved in any significant interaction with the host framework (Fig. 1b and Fig S1) and as a consequence are responsible for the first mass loss observed in the TGA (Fig. S2).

Single crystals of CDPA-DMAP (**2a**) were obtained from EtOAc. As a strong base, DMAP deprotonates CDPA (Fig. 2a, Table 1). The carboxylate oxygen atoms form an interaction with the protonated nitrogen and weaker interactions with the *ortho* and *meta* hydrogen atoms of neighbouring protonated DMAP molecules (Fig. 2b), giving a cyclic interaction with the protonated heteroatom and the *ortho* hydrogens with a $R^3_4(10)$ graph set. The result of this multiple hydrogen bonding is the formation of a charged 2-D network structure (Fig. 2b). Crystallization of CDPA-DMAP from CH_3CN (**2b**) produces crystalline flakes which are not of sufficient quality for single crystal X-ray analysis. Solid-state luminescence studies of EtOAc (**2a**) and CH_3CN (**2b**) (discussed later) show a red shift (λ_{max} at 522 nm, **2a** and 529 nm, **2b**). The powder X-ray diffraction (PXRD) patterns of **2a** and **2b** are different demonstrating that these systems have different structural arrangements in the crystal (Fig. 3) and TGA for **2b** does not show CH_3CN loss (Fig. S3).

Compound **3** was crystallized from CH_3CN (**3a**), MeOH (**3b**) and EtOH (**3c**). **3a** and **3b** form crystalline fibrous materials and **3c** forms thin crystalline plates, none of which were suitable for single crystal X-ray analysis. **3a** becomes dull on exposure to ambient laboratory conditions. In contrast the fibres (**3b**) filtered from MeOH and thin plates (**3c**) obtained from EtOH do not show any colour change even on drying under vacuum.

The PXRD patterns of **3a** before and after the removal of CH_3CN, **3b** and **3c** are provided in Fig. 4. Although less intense, the peak positions in **3a** before and after CH_3CN removal remain the same, indicating that solvent loss has not induced any structural change. The facile loss of CH_3CN from **3a** (Fig S4) gives further support to the suggestion that this solvent is not involved in strong interactions within this chiral host framework. **3b** exhibits a similar PXRD pattern to **3a** but that of **3c** is different and appears to be a polymorphic form of **3a**

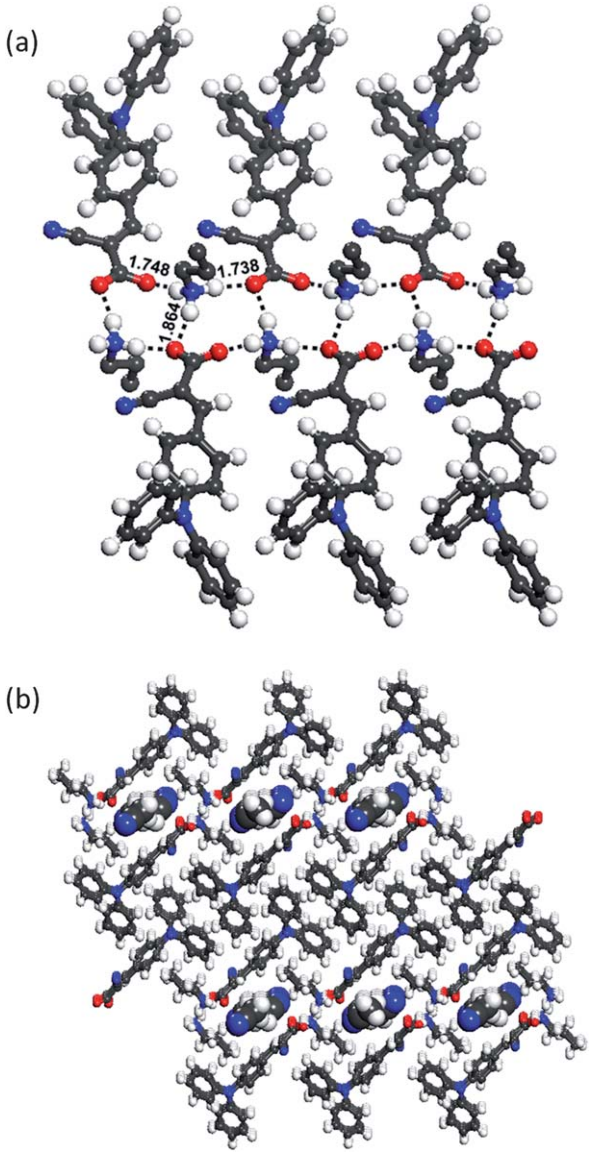


Fig. 1 Selected H-bond interactions in the crystal lattice (a) and crystal packing (b) of **1**. C (grey), N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$ distances (Å) are marked.

and **3b**. Crystallites of **3** obtained from isopropyl alcohol were found to have a similar PXRD pattern to that of **3c**, implying that an increase in the alcohol chain length does not affect the crystal packing. The supramolecular luminescent system **3a**, taken as representative of **3** generally, was examined using circular dichroism spectroscopy to confirm their chirality (Fig. S5).

The presence of amines in the CDPA matrix did not quench the solid-state luminescence and all the supramolecular systems were more intense luminescence than CDPA itself (Fig. S6). The enhancement of the luminescence might be due to the de-aggregation of CDPA in the solid matrix. Supramolecular fibres (**3a**) exhibited the highest luminescent intensity of the three systems investigated. The normalized solid-state luminescence spectra of CDPA, **1** and **2b** are shown in Fig. 5a. Powdered CDPA shows solid-state luminescence at λ_{max} 587 nm which blue shifts to 506

Table 1 Crystallographic data for **1** and **2a**

Compounds	**1** (CCDC-797567)	**2a** (CCDC-797566)
Formula	$[C_3H_{10}N][C_{22}H_{15}N_2O_2]$ $0.5C_2H_3N$	$[C_7H_{11}N_2]$ $[C_{22}H_{15}N_2O_2]$
Formula Wt.	420.01	462.54
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	20.497(8)	7.6459(15)
b/Å	6.687(3)	27.929(6)
c/Å	20.628(8)	11.311(2)
α (°)	90	90
β (°)	118.114(7)	91.84(3)
γ (°)	90	90
V/Å^3	2493.8(18)	2414.3(8)
Z	4	4
D_c/g cm^{-3}	1.119	1.273
T/K	150(2)	150(2)
μ/mm^{-1}	0.072	0.082
2θ range (deg)	50.22	50.50
Total Reflns.	24686	18765
Unique Reflns.	4375	4341
Reflns. used	3394	3723
No. of Parameters	311	320
GOF on F^2	1.083	1.105
Final R1, wR2	0.0834, 0.2298	0.0555, 0.1498

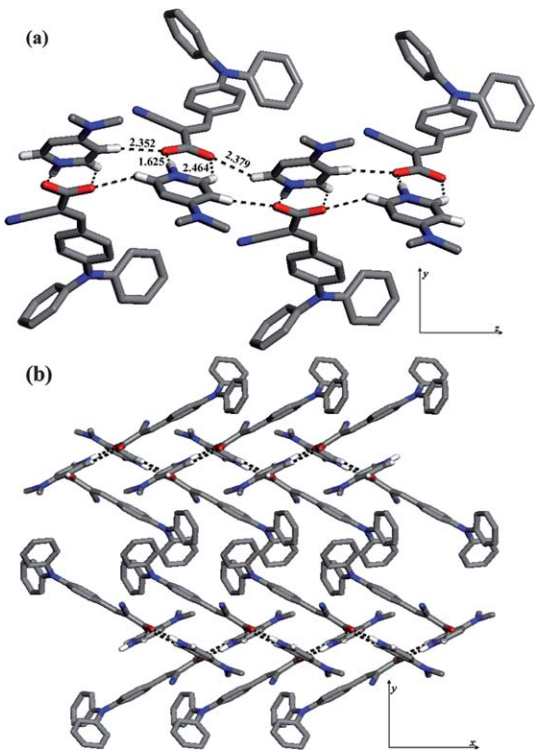


Fig. 2 Selected H-bond interactions in the crystal lattice (a) and crystal packing (b) of **2a**. Only H atoms involved in H-bond interactions are shown; C (grey), N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$ distances (Å) are marked.

nm in the presence of propylamine (**1**). The solvent dependent change in the luminescence of **1** is shown in Fig. 5b. **1** with CH_3CN shows luminescence λ_{max} at 506 nm, whereas on removing CH_3CN (on air-drying for 10 min) the solid-state luminescence shifts to λ_{max} 534 nm. Re-exposure to CH_3CN

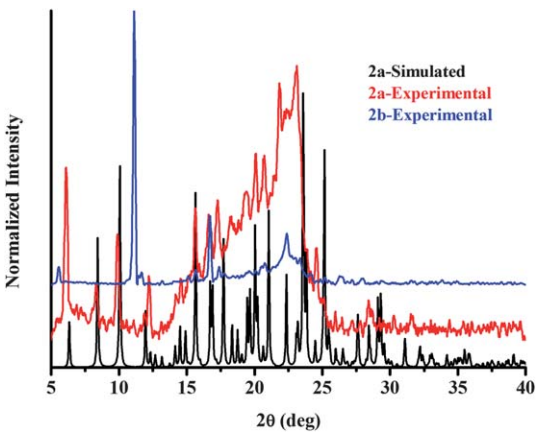


Fig. 3 PXRD patterns of **2a** and **2b**.

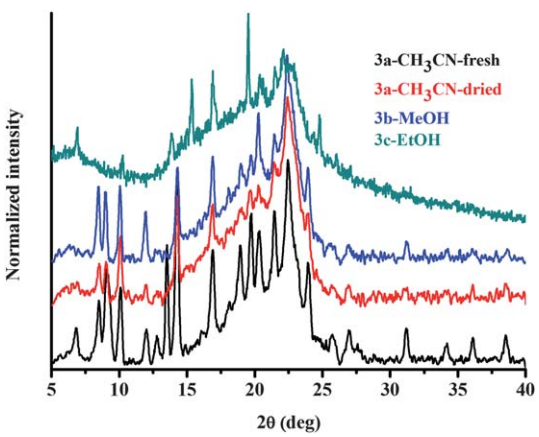


Fig. 4 Solvent dependent PXRD patterns of **3a** and the PXRD patterns of **3b** and **3c**.

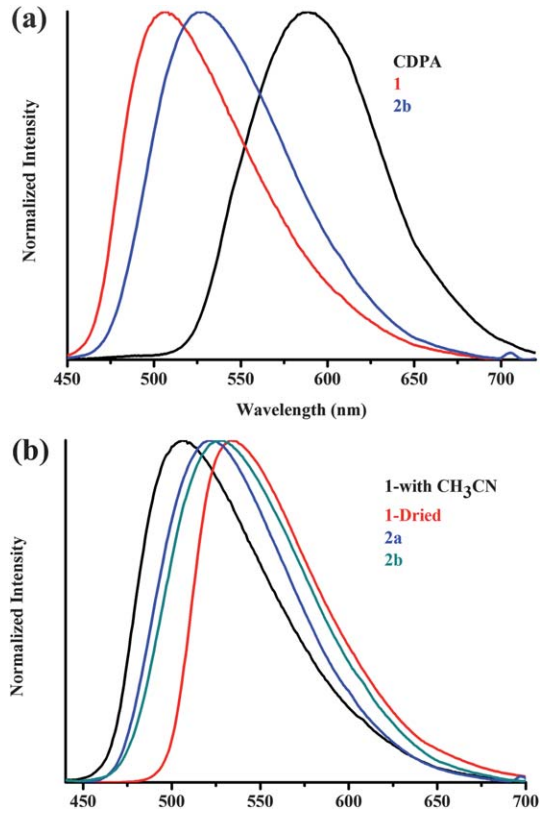


Fig. 5 Normalized solid state luminescence of (a) CDPA, **1**, **2b** and (b) solvent and structural dependent luminescence of **1** and **2** (excitation λ = 370 nm).

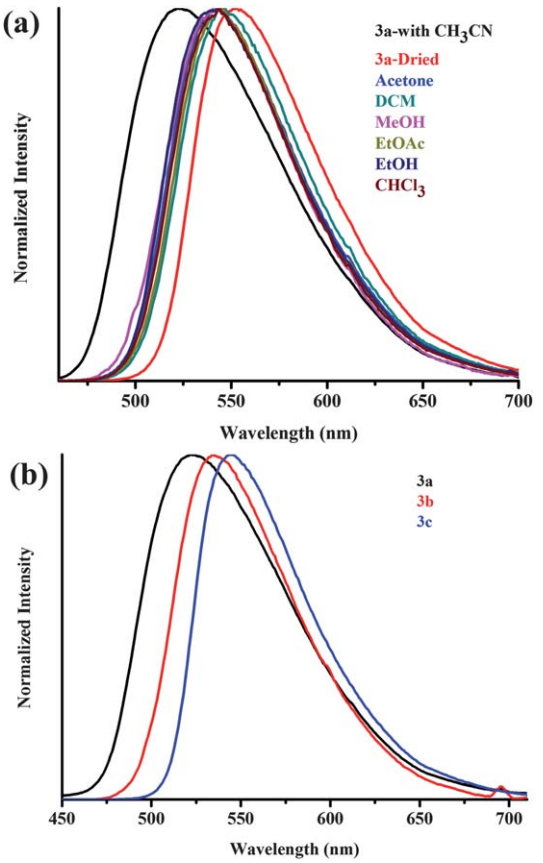


Fig. 6 Normalized solvent dependent solid state luminescence of **3a** (a) and structural dependent luminescence of **3a**, **3b** and **3c** (b) (excitation λ = 370 nm).

switches the luminescence back to λ_{max} 506 nm. Exposure of powdered **1** to other solvent vapours such as EtOAc, CH_2Cl_2, $CHCl_3$, MeOH, EtOH, toluene and H_2O for 5–10 min did not change the luminescence λ_{max} significantly. This gives further support to the selective sensing of CH_3CN within the crystal lattice of **1**.

The different solid forms of **2a** and **2b** show luminescence λ_{max} at 522 nm and 529 nm, respectively (Fig. 5b). Chiral supramolecular luminescent host system **3a**, which changes colour on drying in the air, exhibits selective CH_3CN solvent dependent solid-state luminescence (Fig. 6a). **3a** with CH_3CN luminesces at λ_{max} 523 nm but on removal of CH_3CN (air-drying 5–6 min) red shifts to λ_{max} 553 nm. Re-exposure to CH_3CN vapour (6–8 min) switches the solid-state luminescence back to λ_{max} 522 nm. Since the PXRD patterns of **3a** with and without CH_3CN are the same (Fig. 4), the solid state luminescence switching could be attributed to solvent inclusion in the crystal lattice. The easy removal of CH_3CN from **3a** suggests that CH_3CN does not partake in significant H-bonding interactions in the crystal lattice. Exposure of powdered **3a** to EtOAc, CH_2Cl_2, $CHCl_3$, MeOH, EtOH or acetone solvent vapour for 5–10 min, blue shifts the luminescence λ_{max} to 539–546 nm. The small blue shift of luminescence upon exposure to other solvents might be due to adsorption effects. This observation supports the suggestion of the selective inclusion of CH_3CN in the crystal lattice of **3a**. The elemental analyses for **3** clearly establish the 1 : 1 ratio of CDPA: (1*S*,2*R*)-2-amino-1,2-diphenylethanol in these systems (**3a**, **3b** and **3c**). In addition the analysis shows one included water molecule in each case. The solvent dependency of **3a** and **3b** and polymorphism of **3c** gives rise to different solid state luminescence at λ_{max} 522 nm, 535 nm and 545 nm, respectively (Fig. 6b).

Conclusion

In conclusion, a co-crystallizing approach was used to prepare new supramolecular luminescent host systems, including a chiral luminescent host, based on CDPA. CDPA-propylamine (**1**) and CDPA with (1*S*,2*R*)-2-amino-1,2-diphenylethanol (**3a**) form CH_3CN-selective, supramolecular, luminescent host systems that undergo reversible luminescence changes upon drying and re-exposure to CH_3CN. Interestingly, the crystallization of **3** in different solvents produces species that differ in both structural organization and solid-state luminescence. These results are of interest in sensor applications where the chirality of **3** could be of particular importance.

Acknowledgements

This material is based upon works supported by EU FP6 [MKTD-CT-2004] and Science Foundation Ireland [05PICAI819]. The authors thank the technical assistance of Materials Ireland.

Notes and references

1 (*a*) B. Valeur, *Molecular Fluorescence: Principles and Applications*; Wiley VCH: Weinheim, Germany, 2001; (*b*) J. R. Lakowicz, *Principles of fluorescence spectroscopy*, 3rd ed.; Springer: New York, 2007; (*c*) N. DiCesare and J. R. Lakowicz, *J. Phys.Chem.*, 2001, **105**, 6834; (*d*) K. Rurack, M. Kollmannsberger and J. Daub, *Angew. Chem., Int. Ed.*, 2001, **40**, 385; (*e*) L. Yi, H. Li, L. Sun, L. Liu, C. Zhang and Z. Xi, *Angew. Chem., Int. Ed.*, 2009, **48**, 4034.

2 (*a*) H. S. Joshi, R. Jamshidi and Y. Tor, *Angew. Chem., Int. Ed.*, 1999, **38**, 2722; (*b*) G. Nishimura, H. Maehara, Y. Shiraishi and T. Hirai, *Chem.–Eur. J.*, 2008, **14**, 259; (*c*) J.-P. Desvergne and A. W. Czarnik, *Chemosensors of Ion and Molecular Recognition;* Kluwer: Dordrecht, Vol. 492, 1997; (*d*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609; (*e*) P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71; (*f*) T. Gunnlaugsson, M. Glyn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094; (*g*) E. M. Nolan and S. J. Lippard, *Acc. Chem. Res.*, 2009, **42**, 193; X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qiana and W. Zhua, *Chem. Commun.*, 2010, **46**, 6418.

3 J. Slavīk, *Fluorescence Microscopy and Fluorescent Probes*, Plenum, New York, 1996.

4 (*a*) C.-T. Chen, *Chem. Mater.*, 2004, **16**, 4389; (*b*) G. Barbarella, M. Melucci and G. Sotgiu, *Adv. Mater.*, 2005, **17**, 1581; (*c*) A. Montali, C. Bastiaansen, P. Smith and C. Weder, *Nature*, 1998, **392**, 261; (*d*) Y. Hong, J. W. Y. Lama and B. Z. Tang, *Chem. Commun.*, 2009, 4332.

5 (*a*) F. S. Richardson and J. P. Riehl, *Chem. Rev.*, 1977, **77**, 773; (*b*) J. P. Riehl and F. S. Richardson, *Chem. Rev.*, 1986, **86**, 1.

6 (*a*) K. Yoshida, H. Miyazaki, Y. Miura, Y. Ooyama and S. Watanabe, *Chem. Lett.*, 1999, 837; (*b*) K. Yoshida, Y. Ooyama, S. Tanikawa and S. Watanabe, *Chem. Lett.*, 2000, 714; (*c*) K. Yoshida, Y. Ooyama, S. Tanikawa and S. Watanabe, *J. Chem. Soc. Perkin Trans.*, 2002, **2**, 708.

7 (*a*) Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels and D. Stalke, *Angew. Chem., Int. Ed.*, 2003, **42**, 783; (*b*) J. L. Scott, T. Yamada and K. Tanaka, *New J. Chem.*, 2004, **28**, 447.

8 (*a*) G. R. Desiraju, *Crystal Engineering: the Design of Organic Solids*, Elsevier, New York, 1989; (*b*) H. Dodziuk, *Introduction to Supramolecular Chemistry*, Kluwer Academic Publishers, New York, 2002.

9 Y. Mizobe, M. Miyata, I. Hisaki, Y. Hasegawa and N. Tohnai, *Org. Lett.*, 2006, **8**, 4295.

10 (*a*) Y. Mizobe, N. Tohnai, M. Miyata and Y. Hasegawa, *Chem. Commun.*, 2005, 1839; (*b*) Y. Imai, K. Murata, K. Kawaguchi, T. Sato, R. Kuroda and Y. Matsubara, *Org. Lett.*, 2007, **9**, 3457.

11 S. P. Anthony, S. Varughese and S. M. Draper, *Chem. Commun.*, 2009, 7500.

12 (*a*) Y. Mizobe, T. Hinoue, A. Yamamoto, I. Hisaki, M. Miyata, Y. Hasegawa and N. Tohnai, *Chem.–Eur. J.*, 2009, **15**, 8175; (*b*) N. Nishiguchi, T. Kinuta, Y. Nakano, T. Harada, N. Tajima, T. Sato, M. Fujiki, R. Kuroda, Y. Matsubara and Y. Imai, *Chem.–Asian J.*, 2011, **6**, 1092.

13 (*a*) L. Dobranska, G. O. Lloyd, C. Esterhuysen and L. J. Barbour, *Angew. Chem., Int. Ed.*, 2006, **45**, 5856; (*b*) S. J. Dalgarno, P. K. Thallapally, L. J. Barbour and J. L. Atwood, *Chem. Soc. Rev.*, 2007, **36**, 236; (*c*) M. R. Ams, D. Ajami, S. L. Craig, J.-S. Yang and J. Rebek, Jr, *J. Am. Chem. Soc.*, 2009, **131**, 13190.

14 (*a*) L. Pu, *Chem. Rev.*, 2004, **104**, 1687; (*b*) G. A. Hembury, V. V. Borovkov and Y. Inoue, *Chem. Rev.*, 2008, **108**, 1; (*c*) A. Zehnacker and M. A. Suhm, *Angew. Chem., Int. Ed.*, 2008, **47**, 6970.

15 G. M. Sheldrick, *SADABS, Area Detector Correction*, 2002. Madison, WI, Siemens Industrial Automation, Inc.

16 (*a*) G. M. Sheldrick, *SAINT Area Detector Integration Software*, 1998. Madison, WI, Siemens Industrial Automation, Inc; (*b*) G. M. Sheldrick, *SHELX97 programs for crystal Strucutre Analysis*, (97–2). 1998. *Institüt für Anorganische Chemie der Universität*; (*c*) G. M. Sheldrick, *XPREP. (V5.1)*. 1997. Madison, WI, Bruker Analytical X Ray Systems.

17 A. L. Speck, *PLATON. Acta Crystallogr., Sect. A*, 1990, **A46**, C34.

18 D. P. Hagberg, T. Marinado, K. M. Kalsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt and L. Sun, *J. Org. Chem.*, 2007, **72**, 9550.