# Switching and tuning organic solid-state luminescence *via* a supramolecular approach†

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**Unusual intermolecular interactions of organic luminescent acid, 2-cyano-3(4-(diphenylamino)phenyl)acrylic acid (CDPA), with amines lead to the formation of supramolecular luminescence systems with switchable and tunable solid-state luminescence.**

Organic solid-state luminescent materials have a potential role in a wide range of high-technology applications such as organic light emitting diodes (OLEDs),[1] semiconductor lasers[2] and fluorescent sensors.[3] In particular the switching and tuning of organic solid-state luminescence is of current interest to fundamental research and practical applications. In solution, solvatochromism,[4,5] the addition of metal ions,[5a,6] and the variation of substitution[5] or pH[5a,6,7] lead to the tuning and switching of the luminescence. However organic solid-state luminescence, which is rare due to the aggregation quenching effect, has mostly been tuned by the modification of substitutions on single molecules[8] or the exploitation of polymorphism.[9,10] The latter approach is effective as the optical properties in the solid are controlled by molecular organization but it offers little predictability, the former requires interactive synthetic improvement.

Supramolecular chemistry provides a versatile approach to tuning and switching solid-state luminescence by controlling the molecular organization through weak interactions.[11] For example, solvent dependent solid-state luminescence has been demonstrated by supramolecular host systems generated from the mixing of luminescent organic acids and amines.[12] In general, deprotonation and protonation provides a simple strategy to tune or switch the emission of organic luminescent acids across a wide wavelength range. Furthermore the amine induced manipulation of the acid protons, *via* subtle variations in H-bond formation and controlled deprotonation, creates an opportunity to gradually tune the solid-state luminescence and simultaneously provides a platform for amine sensing. Herein, we report supramolecular luminescence systems based on 2-cyano-3(4-(diphenylamino)phenyl)acrylic acid (CDPA) and amines (pyridine (**1**), pyrrolidine (**2**), piperidine (**3**) and morpholine (**4**)). These systems exhibit blue shifted luminescence compared to the parent acid and in the case of **3** solvent dependent solid-state luminescence was observed.

CDPA was synthesized following the reported procedure[13] and crystallized from $CH_3CN$ by slow evaporation. The single crystal X-ray structure revealed the formation of a helical network generated *via* intermolecular H-bond interactions (O–H···NC) involving the carboxylic proton and cyano nitrogen atom (Fig. 1a).‡ Crystals **1–4** were grown from 1 : 1 molar solutions of the appropriate amine and CDPA in $CH_3CN$. 1 : 0.5 and 1 : 1 CDPA–amine co-crystals were formed in **1** and **2–3**, respectively. Fig. 1b–e show the selective H-bond interactions of **1–4** in the crystal lattice. In **1**, all five pyridine ($pK_a$ = 5.14) protons are involved in intermolecular H-bond interactions with different CDPA molecules. The disordered *para* carbon of pyridine is involved in C–H···O interactions with the carbonyl oxygens of CDPA. The other four pyridine C–H form C–H···NC H-bond interactions with the cyano nitrogen of different CDPA molecules (Fig. 1b). The multiple pyridine interactions coupled with the carboxylic O–H···O–H intermolecular H-bond interactions lead to the formation of CDPA dimers. Thermogravimetric studies reveal the loss of pyridine molecules at high temperature, in support of the presence of multiple H-bond interactions in the lattice (Fig. S3, ESI†).

**2** (pyrrolidine $pK_a$ = 11.27) and **3** (piperidine $pK_a$ = 11.22), containing stronger bases, form only intermolecular H-bonding interactions without deprotonating the carboxylic acid. In **2** the hydrogen atoms of the *meta* carbons on the pyrrolidine form strong C–H···O interactions with the carboxyl oxygens (Fig. 1c). The CDPA carboxylic proton is involved in an intramolecular H-bond interaction with the cyano nitrogen atom (O–H···NC). The pyrrolidine nitrogen atoms, usually active in H-bonding, do not take part in any supramolecular interactions. In **3**, however, the piperidine nitrogen atoms do take part in H-bond interactions with the carboxylic acid: the resulting N–H···O and O–H···N intermolecular H-bond interactions lead to the formation of CDPA dimers. Unexpectedly morpholine ($pK_a$ = 8.36), the weakest base of the alicyclic amines used, deprotonates CDPA in **4**. The ionic NH···O H-bond interactions between the morpholine nitrogen and the carboxylate oxygens of CDPA lead to the formation of CDPA dimers (Fig. 1d). These are further linked by C–H···O interactions between morpholine CH and CDPA carboxylate oxygens into tetramers. Clearly there is a complex balance of forces at play in the solid-state structures which go beyond or over-ride mere solution-based $pK_a$ considerations.

**3** forms a supramolecular luminescent host system by including two $CH_3CN$ molecule in the crystal lattice (Fig. 2); one of which is disordered on single crystal X-ray analysis. Attempts were made to crystallize **1–4** in various solvents to check for the formation of other supramolecular luminescent host systems. **2**, **3** and **4** were found to produce crystals in $CH_3CN$ and EtOAc; EtOAc producing very small crystals. **1**, however, formed a crystalline product only in $CH_3CN$. The

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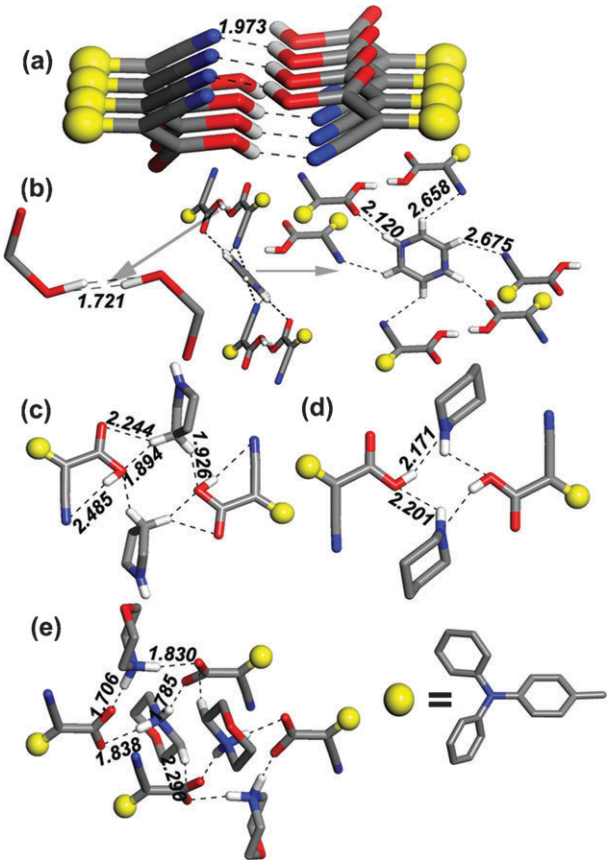


**Fig. 1** Selected H-bond interactions in the crystal lattice of (a) CDPA, (b) **1**, (c) **2**, (d) **3** and (e) **4**. Only H atoms involved in H-bond interactions are shown; C (grey), N (blue), O (red), H (white); H-bonds (broken line). $d_{H\cdots A}$ distances (Å) are marked.

similar powder X-ray diffraction (PXRD) patterns of **2** and **4** obtained from $CH_3CN$ and EtOAc confirmed the same crystal lattice for these systems irrespective of solvent (Fig. S1, ESI†). However in the case of **3** there were distinct differences (before and after the removal of $CH_3CN$ and **3** obtained from EtOAc) suggesting a difference in the crystal structures (Fig. S2, ESI†). This was anticipated given the host–guest inclusion of $CH_3CN$ in the single crystal X-ray structure of **3** (Fig. 2) and was implied by its solid-state luminescence properties (discussed later, Fig. 3b). Thermogravimetric studies support the formation of a supramolecular host system only in $CH_3CN$ and reveal the loss of $CH_3CN$ from **3** and the appropriate amine from **1** to **4** at higher temperatures (Fig. S3, ESI†).

The normalized solid-state luminescence spectra of CDPA and **1–4** are shown in Fig. 3a. The quantum yield ($\Phi_f$) of CDPA, as determined by comparison with coumarin **6**, was 0.165 in $CH_2Cl_2$. The intensity of this luminescence was found to vary very little from that of the solid-state sample. The presence of amines however enhanced the solid-state luminescence intensity of CDPA, *e.g.* a 2-fold enhancement was observed for **3** (Fig. S4, ESI†). This might be due to the deaggregation of CDPA in the solid matrix. Powdered CDPA shows solid-state luminescence at 587 nm which undergoes a gradual blue shift to 494 nm in the presence of amines. The subtle change of carboxylic acid H-bond interactions from O–H···NC in CDPA to O–H···O–H (Fig. 1a and b) in **1** blue

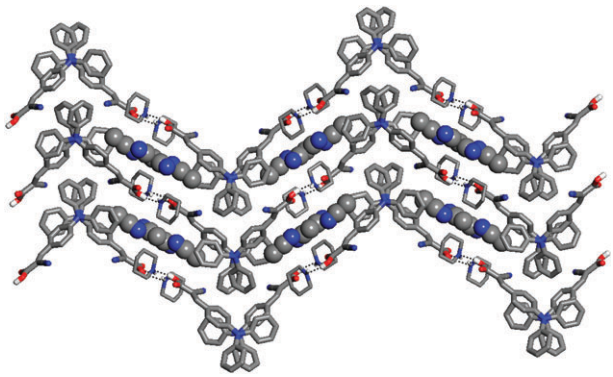

**Fig. 2** Supramolecular luminescent host structure of **3** with $CH_3CN$. $CH_3CN$ are shown in space filling mode. Only H atoms having H-bond interactions are shown; C (grey), N (blue), O (red), H (white); H-bonds (broken line).

shifts the luminescence from 587 nm to 565 nm and the formation of H-bond interactions with pyrrolidine and piperidine further blue shifts the luminescence to 531 and 536 nm (**2** and **3**). The complete deprotonation of CDPA carboxylic acid in **4** results in solid-state luminescence at 494 nm.

The supramolecular luminescent host system **3** might be expected to exhibit solvent dependent solid-state luminescence properties. The $CH_3CN$ was removed from **3** by drying under vacuum for 24 h. The strong H-bond formation of $CH_3CN$ necessitates this long drying time. The solvent dependent change of luminescence of **3** is shown in Fig. 3b. **3** with $CH_3CN$ exhibit luminescence ($\lambda_{max}$) at 536 nm, whereas on removing $CH_3CN$ luminescence ($\lambda_{max}$) occurs at 507 nm. Re-exposure to $CH_3CN$ switches the luminescence $\lambda_{max}$ back to 536 nm. **3** obtained from EtOAc exhibits luminescence ($\lambda_{max}$) at 510 nm. Exposure of EtOAc, $CH_2Cl_2$, $CHCl_3$, MeOH, EtOH, toluene and $H_2O$ solvent vapor on powdered **3** for 3–5 min red shifts the luminescence to 518–522 nm (Fig. S5, ESI†). This observation clearly supports the selective inclusion of $CH_3CN$ in the crystal lattice of **3** as was confirmed by single crystal investigation. No solvent dependence in the solid-state luminescence of **2** or **4** was observed.

Importantly solid-state luminescent switching was demonstrated by the cyclical exposure of powdered CDPA to amines (pyrrolidine, morpholine) and then to immersion in 0.1 M HCl solution for 2 h (Fig. 4). The amine exposure blue shifts the CDPA solid-state luminescence from 587 nm to 531 nm (pyrrolidine) and 494 nm (morpholine). These luminescence $\lambda_{max}$ closely match those of **2** and **4** obtained from $CH_3CN$ solution. The PXRD studies also confirm the conversion of CDPA to **2** and **4** by pyrrolidine and morpholine vapor exposure, respectively (Fig. S6, ESI†). The conversion in morpholine takes considerably longer (2 h) which might be due to the low volatility of morpholine. For both samples, submersion in HCl solution for 2 h results in the reversal of the luminescence signals back to those of powdered CDPA. The PXRD pattern of the HCl solution immersed samples also closely matches that of the simulated PXRD pattern of single crystal CDPA (Fig. S7, ESI†).

In conclusion we have used a supramolecular approach to tune and switch the solid-state luminescence of CDPA. The subtle variation in the H-bond interactions and deprotonation

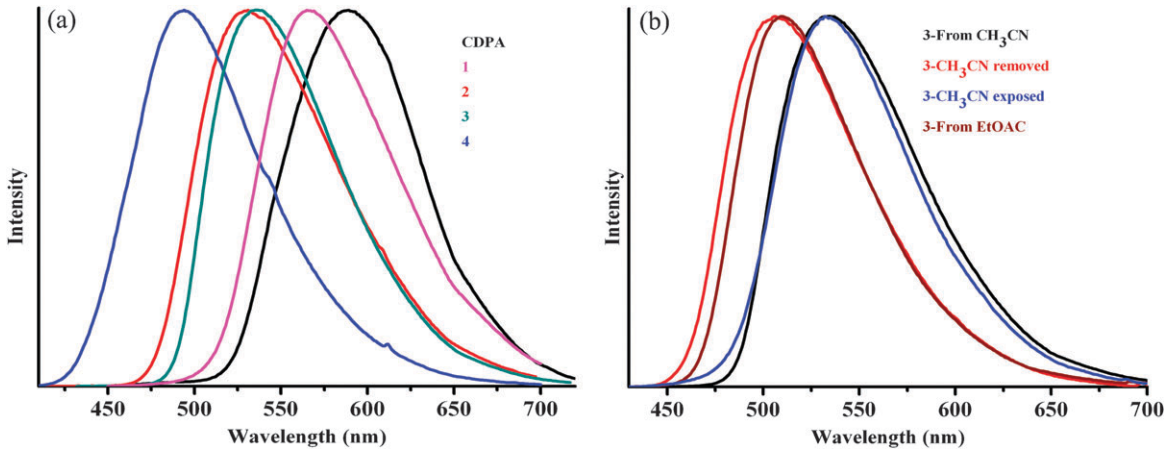


**Fig. 3** Normalized solid-state luminescence of (a) CDPA, **1–4** and (b) solvent dependent luminescence of **3** (excitation $\lambda$ = 370 nm).

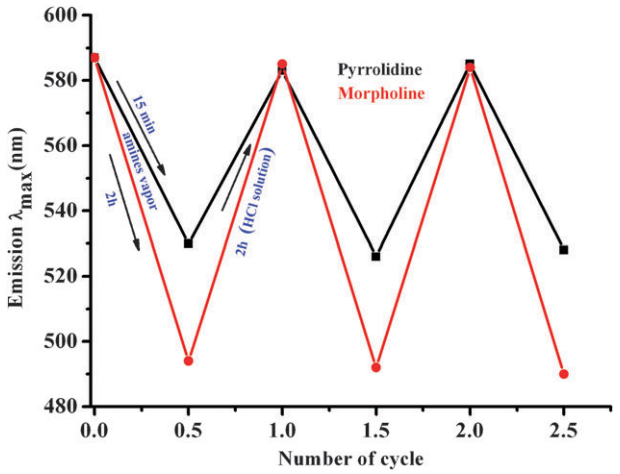


**Fig. 4** Switching of solid-state CDPA luminescence. Arrow indicates the time required for the conversion (excitation $\lambda$ = 370 nm).

leads to the gradual blue shift of CDPA solid-state luminescence from 587 nm to 494 nm. **3** gives a $CH_3CN$ selective supramolecular luminescent host system. Tuning and indeed switching of the luminescence is demonstrated by exposing powdered CDPA to amine vapor (pyrrolidine, morpholine) and HCl solution. Developments of chiral supramolecular luminescent host systems based on CDPA are underway.

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## Notes and references

‡ *Crystal data*: CDPA (CCDC: 737400): $C_{22}H_{16}N_2O_2$, $M$ = 340.37, monoclinic, $P2_1/n$, $a$ = 13.568(1), $b$ = 9.459(1), $c$ = 13.642(1) Å, $\beta$ = 104.167(2), $V$ = 1697.6(3) Å$^3$, $Z$ = 4, $T$ = 150 K, 9595 reflections measured, 2985 unique ($R_{int}$ = 0.0248), final $R$ values: 0.0330, w$R$: 0.0893; **1** (CCDC 737402): 2($C_{22}H_{16}N_2O_2$), $C_5H_5N$, $M$ = 759.84, monoclinic, $P2_1/c$, $a$ = 7.877(1), $b$ = 9.424(1), $c$ = 26.835(3) Å, $\beta$ = 93.023(3), $V$ = 1989.3(4) Å$^3$, $Z$ = 2, $T$ = 150 K, 11 236 reflections measured, 3497 unique ($R_{int}$ = 0.0307), final $R$ values: 0.0553, w$R$: 0.1404; **2** (CCDC 737399): $C_{22}H_{16}N_2O_2$, $C_4H_9N$, $M$ = 411.49, monoclinic, $P2_1/c$, $a$ = 9.461(1), $b$ = 25.424(2), $c$ = 11.161(1) Å, $\beta$ = 125.704(5), $V$ = 2180.0(3) Å$^3$, $Z$ = 4, $T$ = 150 K, 12 692 reflections measured, 3855 unique ($R_{int}$ = 0.0402), final $R$ values: 0.0611, w$R$: 0.1660; **3** (CCDC 737403): 2($C_{22}H_{16}N_2O_2$), 2($C_5H_{11}N$), 3($C_2H_3N$), $M$ = 971.17, orthorhombic, $Pbcn$, $a$ = 32.166(2), $b$ = 9.900(7), $c$ = 16.407(1) Å, $V$ = 5224.4(6) Å, $Z$ = 4, $T$ = 150 K, 53 187 reflections measured, 4686 unique ($R_{int}$ = 0.0287), final $R$ values: 0.0490, w$R$: 0.1398; **4** (CCDC 737401): $C_{22}H_{15}N_2O_2$, $C_4H_{10}NO$, $M$ = 427.49, triclinic, $P\bar{1}$,$a$ = 11.231(1), $b$ = 16.368(1), $c$ = 26.031(2) Å, $\alpha$ = 99.435(1), $\beta$ = 102.219 (1), $\gamma$ = 99.471(2), $V$ = 4514.0(6) Å$^3$, $Z$ = 8, $T$ = 150 K, 49 086 reflections measured, 15 976 unique ($R_{int}$ = 0.0505), final $R$ values: 0.0580, w$R$: 0.1282.


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