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# Mechano-fluorochromic Pt<sup>II</sup> Luminogen and Its Cysteine Recognition

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**Abstract:** A new triphenylamine-based organometallic  $Pt^{II}$  luminogen (1) and its analogous organic compound (2) are reported. The molecules are decorated with aldehyde functionality to improve their photophysical properties by utilising donor–acceptor interactions. The single crystal X-ray structure analysis of  $Pt^{II}$  analogue 1 revealed that the neighbouring molecules were loosely organised by weak intermolecular C–H···π interactions. Because of the twisted nature of the triphenylamine backbone the compounds

# Introduction

The recent years have witnessed a steady growth in the exploration of luminogenic materials due to their potential applications in sensing and optoelectronics.<sup>[1]</sup> Among them a particular type of material has attracted considerable attention owing to its fluorescence switching behaviour between bright and dark states under different external stimuli like mechanical force, heat, exposure to chemicals, etc.<sup>[2]</sup> Stimuli-sensitive compounds are believed to be potential materials for applications in data storage, security inks, sensing, optical switches and in forensic sciences.<sup>[1]</sup>

Although several luminescent molecules are reported in the literature which exhibit stimuli-responsive fluorescence switching in solution, their solid-state fluorescence usually decreases due to an event known as aggregation-caused quenching (ACQ).<sup>[3]</sup> However, new phenomena known as aggregationinduced emission (AIE) and aggregation-induced emission enhancement (AIEE) have also been observed in certain class of materials.<sup>[4,5]</sup> In these compounds the emission intensity enhances upon aggregate formation in solution and also in the solid state.<sup>[6]</sup> Several mechanisms for AIE/AIEE have been proposed, including restriction of intramolecular rotation (RIR), the formation of J-aggregate, intramolecular planarization and restriction of the transition from locally excited state to the twisted intramolecular charge-transfer state.<sup>[6]</sup> Several of the AIE/AIEE materials are also known to be piezochromic and mechanochromic, which makes them suitable candidates for the showed aggregation-induced emission enhancement in THF/water mixture. Due to their loose crystal packing, upon application of external stimuli these luminogens exhibited mechano-fluorochromic behaviour. The crystalline forms of the compounds displayed a more superior emission efficiency than the grinded samples. Moreover, the compounds showed crystallization-induced emission enhancement (CIEE) and exhibited chemodosimetric response towards cysteine under physiological condition.

development of new stimuli-responsive smart materials.<sup>[7]</sup> Along with several new purely organic molecules, a few luminogens containing different metal centres like Zn<sup>II</sup>, Ir<sup>III</sup>, In<sup>III</sup>, Al<sup>III</sup>, Au<sup>I</sup>, Ag<sup>I</sup> and Cu<sup>I</sup> have shown stimuli-responsive fluorescence switching along with AIE or AIEE.<sup>[8–14]</sup> Although several Pt<sup>II</sup> luminogens are reported to exhibit mechanochromic (MC) luminescence due to their variation in morphological packing as well as in Pt–Pt interaction in the solid state, none of them has shown emission enhancement in solution upon aggregate formation.<sup>[15,16]</sup> The fact that there are very few reports on organometallic materials having both mechano-fluorochromic and AIE behaviour indicates the lack of clear guidelines for designing such molecules which can exhibit both these properties together.

Several polyaromatic compounds like pyrene, anthracene, stilbene, silole, carbazole, triphenylamine, etc., have been used in developing stimuli-responsive materials.<sup>[6,7]</sup> The most common feature of MC-luminogens is their twisted aromatic backbone which restricts molecular close-packing by decreasing  $\pi$ - $\pi$  interaction and also enables the molecules to crystallize in a loosely bound manner. Therefore, upon application of external stimuli, the molecular packing in the crystals can undergo severe deformation which is manifested in their change in photophysical properties. In this regard, we focused our attention on the triphenylamine moiety (TPA). To reduce the steric strain among the neighbouring aromatic hydrogen atoms, the TPA moiety is inherently twisted. In the solid state this non-planarity of the TPA core restricts both aggregate and excimer formation by reducing  $\pi$ - $\pi$  interaction. Therefore, TPA is a suitable material, based on which new MC-luminogens can be developed.

It is well known that, crystallization of the luminophores reduces their emission efficiency in solid state due to different detrimental effects including  $\pi$ - $\pi$  interaction, excimer forma-

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tion, etc.<sup>[17]</sup> This effect in solid compounds is known as crystallization-caused quenching (CCQ) which is analogues to ACQ of luminogens in solution. When crystallized, the common organic luminogens show CCQ. Therefore, considerable efforts are being devoted to the fabrication of efficient amorphous thin films of luminogens for their use in optoelectronics. But it is well documented in the literature that crystalline materials have more potential as charge carriers, and therefore, can be used as semiconductors in organic light-emitting diodes (OLED's), organic thin film transistors (OTFTs), etc.<sup>[18]</sup> Recently, compounds with higher emission in their crystalline state have also been reported.<sup>[19]</sup> In comparison to AIE effect of luminogens in solution, this phenomenon is called crystallization-induced emission enhancement (CIEE). Different factors including conformational twisting, structural rigidification by weak intermolecular interactions along with various packing modes of the compounds in solid state are known to control the CIEE efficiency. This efficient emission in crystalline phase makes them attractive candidates to be used in the field of optoelectronics. The previously reported CIEE-active compounds were mostly organic, containing different polyaromatic backbones like diphenylbenzofulvenes, hexaphenylcyclobutane, diketopyrrolopyrole, phosphorous-containing heterocycles, etc. Unlike purely organic luminogens, metal-containing CIEE compounds are rare. Very recently an Au<sup>I</sup> complex with efficient CIEE effect was reported.<sup>[19e]</sup> We decided to use Pt-acetylide with the TPA backbone to develop new luminogens.

Platinum–acetylide derivatives are well known for their extensive use in nonlinear optics, optoelectronics, cellular imaging and high-efficiency electroluminescent devices.<sup>[20]</sup> Our group has previously reported several interesting luminescent molecules with the Pt–acetylide backbone for nitroaromatics detection.<sup>[21]</sup> Although photophysical properties of the Pt<sup>II</sup> derivatives in solution phase are well explored, their solid-state luminescence suffers from ACQ as well as fluorescence quenching due to heavy metal effect.<sup>[22]</sup> We decided to synthesize TPA-based Pt–acetylide compound 1 and its complementary organic compound 2 to investigate and compare their photophysical properties in solution as well as in solid state. Both compounds have a planar central area which can function as the stator; and the terminal phenyl rings of the TPA moiety would behave like rotors.

Some of the previously reported MC-lumiogens which exhibited AIE/AIEE in solution are also found to be more efficient emitters in crystalline phase than their amorphous counterpart, thus, they are CIEE active.<sup>[23]</sup> In our investigation, we found out that both molecules **1** and **2** are highly emissive in their crystalline phase.

In this study, we report the mechano-fluorochromic property of two AIEE-active compounds (1 and 2). To the best of our knowledge, the  $Pt^{II}$  analogue is the first example of mechano-fluorochromic  $Pt^{II}$  luminogen exhibiting CIEE property. Moreover, they exhibited selective chemodosimetric response towards cysteine under physiological condition.

# **Results and Discussion**

#### Synthesis of compounds 1 and 2

Following Sonogashira coupling, **a** was treated with trimethylsilylacetylene along with  $[Pd(PPh_3)_2Cl_2]$  as the catalyst in triethylamine under reflux condition for two days to obtain **b** in approximately 95% yield (Scheme 1). After desilylation of **b** in a solvent mixture of methanol/dichloromethane (MeOH/DCM) at room temperature in the presence of potassium carbonate, **c** was obtained. Finally compound **1** was prepared by the reaction of **c** with *trans*-[(PEt<sub>3</sub>)<sub>2</sub>Ptl<sub>2</sub>] in a mixture of toluene and diethylamine at room temperature for two days. Cul was used as catalyst for this reaction and the yield was approximately 80%. Compound **2** was obtained in 75% yield by Sonogashira coupling of **c** with **a** in triethylamine under reflux condition for two days (Scheme 1).

#### Characterization

The crude compounds were isolated as yellow solids. After purification, the final compounds 1 and 2 were obtained as light and deep yellow solids, respectively. All the compounds were characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, IR and finally by mass spectrometry analysis. Finally, the structure of compound 1 was established from single crystal X-ray diffraction analysis. The crystallographic data of compound 1 are provided in Table 1.

Single crystals of **1** were grown by slow evaporation of a saturated chloroform solution. A block shaped yellow crystal was analysed by X-ray crystallography (CCDC 1414114 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre). The crystal structure of compound **1** is shown in Figure 1.

The torsion angle of the terminal phenyl rings with the central plane is 73.13°. Therefore, the TPA rings are nonplanar and this twisted TPA backbone can have a significant influence on solid state photophysical properties of the compounds. The molecular packing of 1 is illustrated in Figure 2. As expected, the molecules do not show any  $\pi$ - $\pi$  interaction due to the inherently twisted TPA backbone, however, there is a C–H… $\pi$ interaction (d = 2.820 Å) between the  $-PEt_3$  group and the terminal aromatic moiety that acts as a rotor. Also, the terminal aromatic group has a C–H··· $\pi$  (d=2.885 Å) interaction with the alkyne moiety. Therefore, the crystal structure is loosely packed by weak hydrogen bonding. The layers are oriented in fishbone pattern. Upon application of mechanical force the weak interactions can be destroyed and the loosely attached molecules can slip over one another. This structural change can directly influence the luminescence of the molecules in solid state.

#### **Photophysical studies**

The UV/Vis spectra of the compounds were recorded with varying tetrahydrofuran (THF)/water content as water is a poor





Scheme 1. Synthesis of compounds 1 and 2.

Table 1. Crystallographic data and refinement parameters for compound           1.			
Compound	1		
empirical formula	$C_{56}H_{58}N_2O_4P_2Pt$		
F <sub>w</sub>	1080.1215		
<i>T</i> [K]	298		
crystal system	monoclinic		
space group	P21/n		
a [Å]	10.777 (15)		
b [Å]	20.996 (3)		
c [Å]	11.227 (17)		
$\alpha$ [°]	90		
$\beta$ [°]	105.13 (4)		
γ [°]	90		
V [ų]	2452.6		
Ζ	2		
$ ho_{calcd}  [g  cm^{-3}]$	1.462		
$\mu(Mo_{K\alpha}) \ [mm^{-1}]$	0.087		
λ [Å]	0.71073		
F(000)	1096		
no. of collected reflens	7250		
no. of unique reflens	6895		
goodness of fit (F <sup>2</sup> )	0.784		
$R_1 [l > 2\sigma(l)]^{[a]}$	0.1628		
$wR_2 \left[l > 2\sigma(l)\right]^{(b)}$	0.3117		
[a] $R_1 = \Sigma  F_0  -  Fc  / \Sigma  F_0 $ , [b] $wR_2 = (\Sigma [w(F_0^2 - Fc^2) / \Sigma [w(F_0^2 - Fc^2) /$	$\binom{2}{0}^{2}^{2}^{1/2}$ .		



Figure 1. Ball and stick diagram of the crystal structure of compound 1.

solvent for the compounds. Compounds **1** and **2** exhibit broad absorption spectra with maxima centred around 375 and 380 nm, respectively (Figure 3). For compound **1** the absorbance decreases with increasing water fraction. A 20 nm red shift (375 to 395 nm) was observed when the water fraction was 70% (Figure 1). Level-off tails were observed at water fraction higher than 60%. Such tails are proposed to originate from Mie scattering effect which is generally developed when spherical nanoaggregates are formed in the medium.<sup>[24]</sup> For compound **2** also the emission maxima at 380 nm decreased

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Figure 2. Molecular packing of 1 in crystalline state.

and at 70% water fraction a new peak at 400 nm was observed (see the Supporting Information).

The fluorescence spectra of the compounds were recorded in THF/water mixtures with varying water fraction. The compound **1** exhibited a broad spectrum with maximum at 500 nm in 10% water/THF mixture. With increasing water content the peak intensity gradually decreased, but at 70% water fraction a new high-intensity peak appeared at  $\lambda_{max}$ =510 nm. The sixfold enhancement of fluorescence intensity is proposed to be due to the aggregation of the molecules at higher water portion. When more water was added the peak intensity slightly decreased (Figure 1). The initial emission intensity of compound **2** also decreased upon increasing water content in the solvent system, but increased above 70% water fraction (see the Supporting Information). At lower water fraction the peak maxima at 480 nm decreased, but a new peak at 500 nm appeared at 70% water fraction. Compounds 1 and 2 showed six- and twelvefold enhancement in emission intensity, respectively. When further water was added to the systems the fluorescence intensity decreased. Thus, these compounds exhibited aggregation-induced emission enhancement (AIEE) behaviour. As observed in the previously reported AIE/AIEE materials, we speculate that in dilute solutions of the compounds the excited state energy was dissipated by the rotational motion of the terminal phenyl rings.<sup>[6]</sup> Thus, the solution-state luminescence was negligible. When water was added to the solution, aggregates were formed due to poor solubility of the compounds in water. Upon aggregate formation the molecules were tightly packed in a very confined space. Therefore, excitation energy release through non-radiative decay processes, like torsional motion of the phenyl rings were restricted. The molecules released the excited state energy in a radiative decay pathway only, and as a result the fluorescence intensity increased. Therefore, the compounds showed higher fluorescence in aggregate forms.

We think that the molecules slowly organize in an ordered crystalline aggregate when the water content is moderate (70%), but upon addition of excess water the molecules formed random amorphous aggregates with lower fluorescence intensity.<sup>[25]</sup> Careful inspection of the fluorescence spectra revealed that the ordered aggregates were more efficient emitters than the amorphous analogues.

Dynamic light scattering experiments with the samples in the aggregate state were performed, which revealed the spherical nature of the aggregates for both compounds



Figure 3. Absorption spectra of 1 in THF/water mixture (top left) and fluorescence spectra (top right) in THF/water mixture. Excitation wavelength = 375 nm. Compound 1 (concentration  $10^{-5}$  mol  $L^{-1}$ ) with varying amount of water fractions under 365 nm UV light in THF/water mixture.

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(Figure 4). For compound **1** the average particle size was around 152 nm and for compound **2** it was about 120 nm in diameter. Finally scanning electron microscopy (SEM) of the aggregates coated on the carbon tapes was performed to examine the spherical shapes of the aggregates. For compound **1** well distinguishable spherical particles of about 150 nm in diameter were obtained and for compound **2** the size was approximately 120 nm.



Figure 4. a) Particle size distribution of the aggregate of 1 in 70% water/THF mixture by DLS experiments, and b) SEM image of 1 drop-casted on carbon tape.

# Crystallization induced emission enhancement of compounds 1 and 2

Crystallization normally reduces emission intensity of common fluorophores due to the detrimental effect of  $\pi$ - $\pi$  interaction and excimer formation. Therefore, luminogens the crystalline forms of which are better emitters than amorphous analogues will have a better prospect in optoelectronics. To verify whether the crystals of 1 have higher fluorescence than the grinded powder form, single crystals of 1 were grown by slow evaporation of saturated chloroform solution. The powder sample was prepared by thorough grinding of the crystals with mortar and pestle. The crystalline and powder samples were characterized



Figure 5. a) Solid-state emission spectra of crystalline, grinded and DCM fumed samples of 1, and b) their PXRD patterns.

by powder X-ray studies. The crystallinity of the samples was proven by sharp and intense peaks and the powdered sample exhibited weak and broad peaks (Figure 5).

Upon photoexcitation at 375 nm the crystals of **1** displayed yellow fluorescence with a peak centred at 530 nm, but the powdered sample exhibited faint yellow light at 520 nm (Table 2). The quantum yield of the crystalline sample ( $\Phi_F$  = 38.76%) is eightfold higher than that of the powdered sample ( $\Phi_F$  = 4.52%).

Table 2. Photophysical data of compounds 1 and 2.				
Compound	$\lambda_{abs}$	$\lambda_{em}$	$\phi$ (solid)	$\phi$ (soln)
1	375	510	0.38 (cryst) 0.04 (amor)	0.57 (THF/water)
2	380	500	0.46 (cryst) 0.05 (amor)	0.65 (THF/water)

Therefore, it is evident that compound 1 exhibited crystallization-induced emission enhancement (CIEE). For compound 2 the grinded sample displayed a faint emission at 525 nm, but the crystalline phase was highly emissive with maximum intensity at 530 nm (see the Supporting Information). Therefore, both materials showed variation in solid-state emission when mechanical force was applied. Hence, both the materials were





mechano-fluorochromic (MC). Tuning the emission intensity of mechano-fluorochromic materials due to transition from crystalline to amorphous state by different forces like grinding, pressure, etc., is an active field of research.<sup>[12]</sup> Solvent fumigation is another process that induces crystallization from amorphous/powder materials. Thus, to explore the reversibility of the MC-materials from amorphous/powder to crystalline phase, the grinded powder form of compound 1 was treated with DCM vapour (Figure 5 and Figure 6). The powder XRD pattern of the DCM-treated sample was found to be almost identical with the crystalline material, although the diffraction peaks slightly decreased in intensity. Thus, it is clear that solvent treatment and grinding can reversibly alter the states between highly emissive crystalline phase and poorly emissive pseudoamorphous phase. For compound 2 also similar reversible fluorescence switching behaviour was observed when the grinded sample was exposed to DCM vapour (see the Supporting Information).



Figure 6. Images of the crystalline, grinded and DCM-fumed samples of 1 under UV light (256 nm).

The crystal structure of 1 was examined to explore different weak interactions which might help molecular packing. In dilute solution and in the grinded state the twisted terminal phenyl rings acted as rotors. After photoexcitation, energy was dissipated through a non-radiative pathway by the torsional motion of the phenyl rings. In crystalline form (before grinding), the intermolecular weak interactions restricted the torsional motion of the rings by different weak C–H··· $\pi$  interaction as discussed before. Due to such restricted motion of the rotors, the excited state energy was released by radiative decay process only. Therefore, the crystalline forms are more emissive than the grinded forms. These weak intermolecular interactions not only restrict movement of the terminal phenyl ring but also facilitate the loose packing of 1 in the solid state (Figure 2). Upon application of mechanical force (grinding), the molecules can slip along their long axis to form a metastable poorly crystalline phase, where the weak interactions are mostly absent; and thus the energy decay by the torsional motion of the phenyl rings become prominent.

Several attempts to obtain suitable single crystals of compound **2** were unsuccessful. Therefore, we calculated the energy optimized structures of both the compounds (**1** and **2**) for a comparative study to further elucidate the CIEE mechanism. When compared to already obtained single crystal X-ray

structure, the energy-optimized structure of 1 showed identical geometry with terminal triphenylamine rings twisted out of the plane of the central benzene ring. The dihedral angle of  $70.58^{\circ}$  is very close to the value obtained from single crystal Xray analysis which is 73.13° for 1 (Figure 7). Therefore, we propose that the terminal phenyl rings of 2 will also be twisted out of the central phenyl ring and the dihedral angle was calculated to be 71.11°. As explained earlier this twisted character of the TPA benzene rings restricted aggregate formation in the solid state. Also, the weak intermolecular interactions between the benzene rings helped to prevent the non-radiative decay process by torsional motion. The energy optimized geometry of compound 2 also furnished similar twisted geometry. Thus, we speculate that due to similar geometrical features like 1, compound 2 also exhibited CIEE behaviour in solid and AIEE behaviour in solution.



Figure 7. Geometry-optimized structures of the compounds with side view (top) and top view (bottom), compound 1 (left) and compound 2 (right).

#### Vapochromism

From the fluorescence experiments and quantum yield measurement, it became evident that the crystalline forms of the compounds are better emitters than their grinded forms. The effect of DCM vapour on the grinded powder forms of the materials encouraged us to explore the possibility of using them as potential substrates to sense volatile organic chemicals (VOC).

Recognition of volatile solvents like DCM or chloroform is important for environmental and social safety. When the powder sample of **1** was exposed to different solvents like DCM, chloroform, tetrahydrofuran (THF), hexane and methanol (MeOH), emissions of different intensity with different peak maxima were obtained (Figure 8). Fumigation with hexane and MeOH showed emission maxima centred at 505 nm with different intensity, for chlorinated solvents CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> the maxima were around 520 nm and in THF it was at 532 nm. Therefore, vapour infusion induced emission intensity showed a broad range of 30 nm. Compound **2** also exhibited similar characteristics upon exposure to different solvent vapours (see the Supporting Information).

The fluorescence switching by grinding and vapour exposure was repeated several times for these compounds. Such change in photophysical properties is presumably due to the change in the crystalline forms of the compounds.

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Figure 8. Vapochromism of 1 after exposure to different solvent vapours.

#### **Cysteine sensing**

The interesting effect of structural rigidity on the photophysical properties of compounds 1 and 2 prompted us to explore the materials as sensors. In this context, one of the essential amino acid, cysteine caught our attention. Cysteine is known to have a vital role in protein synthesis and cellular detoxification.<sup>[26]</sup> Low cysteine levels in blood plasma is linked with different conditions, such as liver damage, hair depigmentation, skin lesions, lethargy.<sup>[27]</sup> Excess cysteine in body is reported to be associated with neurodegenerative diseases such as Alzheimer's and Parkinson's disease and also different cardiovascular diseases.<sup>[28]</sup> Therefore, considerable effort has been given for the development of sensitive and selective sensors for cysteine. Fast response time and emission enhancement upon analyte binding are some of the most crucial characteristics of an efficient sensor. Also, designing a sensor for selective detection of a single amino acid is a significant challenge. Among several reported procedures, including thiol-induced cleavage, cyclization of amino-thiol with aldehydes, Michael-type addition reaction and ligand exchange, we chose to explore the chemodosimetric approach by thiazolidine ring formation for cysteine detection.<sup>[28]</sup> The first chemodosimetric approach for cysteine detection was reported by Rusin, Strongin et al.<sup>[30]</sup> Subsequently, several different chemodosimeters with different fluorophore backbones have been reported.<sup>[31]</sup> Our molecules contain an aldehyde group on the terminal phenyl rings. We speculated that the thiazolidine ring formation would restrict the torsional movement of the terminal phenyl rings leading to enhanced luminescence.

For practical application water compatibility as well as sensitivity at physiological pH is essential for a fluorescence sensor. Therefore, for all the photophysical experiments DMF/HEPES buffer was chosen as the solvent. Upon gradual addition of cysteine, a new band was observed centred at 300 nm at the expense of the 375 nm band for compound **1**. The data were recorded after 30 min of cysteine addition to the sensor at room temperature. Compared with other amino acids no new absorption band was observed (Figure 9). Similarly for compound **2** a new peak at around 315 nm appeared and the original peak intensity at 380 nm decreased with increase



Figure 9. Absorption spectral changes of 1 upon gradual addition of cysteine (top) and absorption spectra of 1 with various other amino acids (bottom) in DMF/HEPES buffer (pH 7.4, 4:1, v/v).

in cysteine concentration. Compound **2** also exhibited high selectivity towards cysteine in the presence of other amino acids (see the Supporting Information). Therefore, the compounds are quite selective towards cysteine.

In the emission spectra, a new peak with maxima at 410 nm appeared upon incremental addition of cysteine solution to **1** (Figure 10). The emission enhancement can be attributed to the thiazolidine ring formation upon reaction of cysteine with the terminal aldehyde groups along with ICT turn-off process of the aldehyde. When compared with other amino acids, no new peaks were observed (Figure 10). When the fluorescence response of **2** was examined in the presence of cysteine, a new emission peak appeared at 420 nm. Compound **2** was also found to be highly selective for cysteine.

When the interference of other amino acids on the sensitivity of **1** towards cysteine was monitored, only glutathione (GSH) exhibited minor influence (Figure 11). A similar response was also observed when compound **2** was treated with cysteine in the presence of other amino acids (see the Supporting Information).

For practical application paper-strip-based sensors are favoured due to their low production cost and fast response time.

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**Figure 10.** Fluorescence spectral changes upon addition of cysteine to compound **1** (top) and fluorescence intensity change in the presence of GSH (bottom) in DMF/HEPES buffer upon excitation at 310 nm.



**Figure 11.** Fluorescence responses of 1 towards cysteine in the presence of various amino acids in DMF/HEPES buffer after excitation at 310 nm. Black bars represent the intensity after addition of various amino acids to the stock solution of 1. Red bars represent the intensity upon further addition of cysteine to that solution.

Test strips of compound 1 were prepared by immersing filter paper ( $\approx 1 \text{ cm}^2$ ) in a saturated solution of 1 in DCM followed by vacuum drying. Saturated solutions of different amino acids were drop casted by glass capillary and were air dried. Only for cysteine a blue fluorescent spot was obtained which indicated the usefulness of paper strips for fast detection of cysteine (Figure 12).



Figure 12. Paper strips of compound 1: a) before, and b) after addition of amino acids, illuminated under 365 nm UV/Vis lamp.

The mechanism of cyclized ring formation was also monitored by <sup>1</sup>H NMR spectroscopy. When the partial NMR of compound **2** and its cysteine adduct were compared, the aldehyde peak at 9.91 ppm vanished and two new peaks appeared at 5.48 and 5.65 ppm, which were assigned to the protons of thiazolidine diastereomer (Figure 13). From control experiments with other amino acids it was observed that compounds **1** and **2** were quite selective for cysteine.



Figure 13. <sup>1</sup>H NMR spectra of 2 (above) and its cysteine adduct (below) in  $[D_6]DMSO$ .

# Conclusions

In summary, we report here the mechano-fluorochromic behaviour of two AIEE-active compounds having a triphenylamine backbone. One of them contains  $Pt^{II}$  in the backbone while the other is an organic analogue. The compounds also turned out to be crystallization-induced emission active. The presence of weak intermolecular hydrogen bonding and  $C-H\cdots\pi$  interactions in the crystalline forms were responsible for the abovementioned fascinating optical behaviour. Both compounds also displayed variation in fluorescence intensity upon exposure to different solvent vapours. Therefore, they are potential materials for the development fast responsive sensors for the detection of trace amounts of toxic solvents. The compounds

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were also found to be selective for the detection of cysteine in the presence of several other amino acids under physiological conditions.

### **Experimental Section**

#### Materials and methods

All the reactions were carried out under N<sub>2</sub> atmosphere by using standard Schlenk technique unless stated otherwise. All the starting materials and reagents were purchased from commercially available sources and were used without further purification. Compound a was prepared following the procedure described in the literature.<sup>[32]</sup> The NMR spectra were recorded using a 400 MHz NMR spectrometer. The chemical shifts ( $\delta$ ) in <sup>1</sup>H NMR are reported in ppm relative to Me<sub>4</sub>Si as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvents: CDCl<sub>3</sub> (7.26) and [D<sub>6</sub>]DMSO (2.50). <sup>13</sup>C NMR spectra were recorded at 100 MHz, and the chemical shifts ( $\delta$ ) are reported in ppm relative to external CDCl<sub>3</sub> and [D<sub>6</sub>]DMSO at 77.8–77.2 ppm and 40.50 ppm, respectively. The <sup>31</sup>P NMR spectra were recorded at 120 MHz and the chemical shifts ( $\delta$ ) are reported in ppm relative to external 83% H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm. Electrospray ionization mass spectra were recorded using Esquire 3000 plus ESI mass spectrometers. Electronic absorption spectra and emission spectra were recorded on a LAMBDA 750 UV/Vis spectrophotometer and Horiba Jobin Yvon made Fluoromax-4 spectrometer. For absorption and emission studies, solutions were prepared using a microbalance and volumetric glassware and charged into quartz cuvettes. For solid state vapour exposure studies similar amounts of the compounds (in grinded form) were exposed to different solvent vapours under a closed system and then the spectra were recorded using quartz plate and solid state fluorescence holder. Single crystal X-ray diffraction data were collected on a Bruker D8 Quest diffractometer with CMOS technology. The structure was solved by direct methods using SHELX-97.<sup>[33]</sup> The absolute fluorescence quantum yields were measured by Quanta- $\phi$  Horiba instrument. Timeresolved fluorescence measurements were carried out on an IBH-Data station platform using 370 nm nano-LED source. Dynamic light scattering (DLS) measurements were performed on the zetaseizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He-Ne laser ( $\lambda = 633$  nm). The THF/water mixtures with various water fractions were prepared by slowly adding ultrapure water into the THF solution of samples. The SEM image was obtained using Zeiss Ultra-55 SEM instrument with the sample coated on a carbon tape.

#### Synthesis of b

A flame-dried 100 mL two-neck round bottom flask was charged with **a** (2.00 g, 5.26 mmol), Cul (0.03 g, 0.15 mmol), PPh<sub>3</sub> (0.13 g, 0.52 mol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.18 g, 0.26 mmol) in freshly distilled triethylamine (40 mL) under nitrogen atmosphere and heated for 15 min at 50 °C. Trimethylsilylacetylene (2.5 mL, 15.77 mmol) was added dropwise to the mixture under high nitrogen flow and the reaction mixture was refluxed for 36 h. The solvent was removed under vacuum and the crude was purified by column chromatography using 20% ethyl acetate (EA)/hexane (20%) mixture to afford the product as yellow solid in 95% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =9.90 (s, 2 H), 7.78 (d, *J*=8 Hz, 4 H), 7.46 (d, *J*=8 Hz, 2 H), 7.18 (d, *J*=8 Hz, 4 H), 7.08 (d, *J*=8 Hz, 2 H), 0.25 ppm (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =190.97, 152.06, 146.04, 134.14, 132.18, 131.84, 126.47, 123.75, 120.92, 104.60, 95.77, 0.39 ppm.

#### Synthesis of c

A mixture of compound **b** (2.00 g, 5.31 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.78 g, 20.12 mmol) was dissolved in a solvent mixture of dichloromethane (DCM) and methanol (MeOH) (20:30; v/v) and stirred for 24 h. The solvents were removed under reduced pressure and the crude was purified by column chromatography using DCM/hexane (1:4) as eluent to obtain a yellow solid in 70% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 9.89 (s, 2H), 7.78 (d, *J* = 8 Hz, 4H), 7.48 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 4H), 7.10 (d, *J* = 8 Hz, 2H), 3.11 ppm (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.97, 152.03, 146.39, 134.29, 132.23, 131.86, 126.47, 123.84, 119.77, 83.33, 78.51 ppm.

#### Synthesis of 1

To a freshly distilled mixture of toluene (30 mL) and diethylamine (15 mL) in a Schlenk flask were added c (0.80 g, 2.46 mmol), trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>l<sub>2</sub>] (0.68 g, 0.98 mmol), Cul (0.03 g, 0.19 mmol) and the flask was degassed under vacuum and refilled with nitrogen three times. The reaction mixture was stirred for 48 h at room temperature. The solvent was removed under vacuum and the crude was purified by column chromatography using ethyl acetate/hexane (1:1) as eluent to afford 1 as light yellow solid in 80% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.88$  (s, 4 H), 7.76 (d, J = 8 Hz, 8 H), 7.27 (d, J=8 Hz, 4H), 7.19 (d, J=8 Hz, 8H), 6.70 (d, J=8 Hz, 4H), 2.19 (m, 12 H), 1.25 ppm (m, 18 H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$ 190.94, 152.35, 142.66, 132.92, 131.73, 131.66, 127.39, 127.15, 123.12, 109.18, 60.84, 16.87, 8.85 ppm;  $^{31}\mathrm{P}\;\mathrm{NMR}$  (120 MHz,  $\mathrm{CDCl}_3$ ):  $\delta =$  11.31 ppm; IR:  $\tilde{\nu} =$  2931 (w), 2104 (s), 1690 (s), 1575 (s), 1494 (s), 1275 (m), 1210 (m), 1156 (s), 821 cm<sup>-1</sup> (s); HRMS (ESI):  $C_{56}H_{58}N_2O_4P_2Pt$ ,  $[M+H]^+ = 1081.1295$  (calcd) found: 1081.3704 (100%); elemental analysis calcd [%] (vacuum dried sample) for  $C_{56}H_{58}N_{2}O_{4}P_{2}Pt\colon C$  62.27, H 5.41, N 2.59; found: C 62.87, H 5.34, N 2.93; melting point range: 210–215 °C.

#### Synthesis of 2

A flame-dried 100 mL two-neck round bottom flask was charged with c (0.32 g, 1.00 mmol), Cul (0.005 g, 0.03 mmol), PPh<sub>3</sub> (0.02 g, 0.10 mol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.03 g, 0.05 mmol) in freshly distilled triethylamine (40 mL) under nitrogen atmosphere and heated for 15 min at 50 °C. Compound b (0.57 g, 1.5 mmol) was added to the mixture under high nitrogen flow and the reaction mixture was refluxed for 36 h. The solvent was removed under vacuum and the crude was purified by column chromatography using 40% (v/v) ethyl acetate (EA) and hexane mixture to afford deep yellow solid product in 75% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 9.91$  (s, 4H), 7.80 (d, J=8 Hz, 8 H), 7.52 (d, J=8 Hz, 4 H), 7.22 (d, J=8 Hz, 8 H), 7.14 ppm (d, J = 8 Hz, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 190.59$ , 151.75, 145.73, 133.39, 131.97, 131.53, 126.25, 123.53, 120.43, 89.69 ppm; IR:  $\tilde{v} = 2726$  (w), 1684 (s), 1585 (s), 1503 (s), 1316 (m), 1269 (m), 1211 (s), 1161 (w), 823 cm<sup>-1</sup> (s); HRMS (ESI):  $[M+H]^+ =$ 625.7040 (calcd); found: 625.6950 (100%); elemental analysis calcd [%] (vacuum dried sample) for C<sub>42</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>: C 80.75, H 4.52, N 4.48; found: C 80.43, H 4.43, N 4.21; melting point range: 220–225 °C.

#### Synthesis of nanoaggregates

Initially, stock solutions  $(10^{-3} \text{ M})$  of both 1 and 2 were prepared using spectroscopy grade THF. The required amounts of the aliquots from the stock solutions were transferred to 4 mL glass vials. After addition of an appropriate amount of THF for dilution, distilled water was added to the solutions under vigorous stirring to afford  $(10^{-5} \text{ M})$  solutions with varying water/THF ratio (10-90%).

The photophysical studies were carried out immediately. For SEM analysis 10  $\mu L$  of the aggregate solutions were drop-casted on 1 cm  $\times$  1 cm carbon tape and dried under vacuum for 6 h.

#### **CIEE study**

For CIEE study 20 mg of crystals of sample **1** was taken and its solid state fluorescence was measured. The crystalline sample was recovered and ground thoroughly using mortar and pestle. Powder X-ray diffraction pattern of the grinded sample was analysed before solid-state fluorescence measurement. To verify the reversibility of the sample, the amorphous sample was exposed to DCM vapour for 30 min in a sealed container. The solid-state fluorescence of the solvent treated sample was almost similar to the crystalline phase. This process of grinding and solvent treatment was repeated several times to obtained consistent values. Compound **2** also showed similar reversible mechanochromic behaviour (see the Supporting Information).

#### Fluorescence quantum yield measurement

Fluorescence quantum yields in solution state were calculated using Equation (1) where anthracene ( $\phi$ =0.36 in cyclohexane)<sup>[34]</sup> was used as a reference sample. Here  $\phi_m$  and  $\phi_r$  are the radiative quantum yields of the compounds and reference, respectively;  $A_m$  is the absorbance of the compound and  $A_r$  is the absorbance of the reference;  $D_m$  is the area of emission of the compound and  $D_r$  is the area of emission of the reference and  $N_m$  and  $N_r$  are the refractive indices of the compound and reference solution:

$$\phi_{\rm c} = [\phi_{\rm r}\{(1-10^{-{\rm Ac}}) \times N_{\rm c}^{2} \times D_{\rm c}\}]/\{(1-10^{-{\rm Ac}}) \times N_{\rm r}^{2} \times D_{\rm r}\}$$
(1)

For solid-state quantum yield measurement 100 mg of solid samples were kept on the sample holder and used directly in the instrument to obtain absolute quantum yield.

#### Cysteine sensing

To perform the cysteine sensing under physiological condition, DMF/HEPES buffer (10 mm, pH 7.4, 4:1, v/v) was chosen as solvent. An aliquot (20  $\mu$ L) of the stock solution (10<sup>-3</sup> m) of 1 in DMF was diluted with an appropriate amount of solvent to afford a final solution (10<sup>-5</sup> m). The final solution (2 mL) was taken in a quartz cuvette for cysteine sensing studies. To this solution, a previously made cysteine stock (10<sup>-3</sup> m in water) was added gradually. After addition of cysteine, the solution was stirred at room temperature for 30 min and kept for a further 10 min at 37 °C before recording the data each time. For compound **2**, a similar procedure was followed. For the <sup>1</sup>H NMR spectroscopy data, an appropriate amount of **2** was added to an ethanol solution of cysteine and stirred, overnight. The precipitate obtained was washed with ethanol several times, then dried and NMR spectra were recorded in [D<sub>6</sub>]DMSO.

#### **Computational methodology**

Full geometry optimizations were carried out using Gaussian 09 package.<sup>[35]</sup> The hybrid B3LYP functional has been used in all calculations, mixing the exact Hartree–Fock-type exchange with Becke's expression for the exchange functional<sup>[36]</sup> and that proposed by Lee–Yang–Parr for the correlation contribution.<sup>[37]</sup> The 6-31G basis set was used for all calculations. For compound **1** LanL2DZ basis set was used due to Pt centre.

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