# Macrocycles |Hot Paper|

# Aggregation-Induced Emission of Platinum(II) Metallacycles and Their Ability to Detect Nitroaromatics

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**Abstract:** Two new acceptors containing platinum–carbazole (1) and platinum–triphenylamine (2) backbones with bite angles of 90° and 120°, respectively, have been synthesised and characterised. Reactions of the rigid acceptor 1 with linear dipyridyl-based donors (3 and 4) generated [4+4] self-assembled molecular squares (5 and 6), and similar treatments with acceptor 2 instead of 1 yielded [6+6] self-assembled molecular hexagons (7 and 8). The metallacycles were characterised by multinuclear NMR spectroscopy (<sup>1</sup>H and <sup>31</sup>P) and ESI-MS. The geometries of the metallacycles were opti-

# Introduction

Over the years, luminescent compounds have advanced from being simple chemosensors to smart materials for bioimaging, optoelectronic materials, non-linear optics, and so forth.<sup>[1]</sup> Several new materials with tuneable photophysical properties, including high photostability, intense absorption and sharp and strong emission, have been developed.<sup>[2]</sup> Common fluorophores are highly luminescent in solution, but, when concentrated or solidified, their emission quenches due to excimer/exciplex formation through intermolecular interactions.<sup>[3]</sup> This phenomenon is commonly referred as aggregation-caused quenching (ACQ). Luminescent films with properly organised molecules are a basic requirement for materials used as emissive layers in optoelectronic devices. Conventional fluorophores are not preferred as light sources due to ACQ. A new class of solid emissive materials have emerged that work on the principle of aggregation-induced emission (AIE).<sup>[4]</sup>

Materials that exhibit intense luminescence in solution and in the solid state are highly desirable. Several new approaches involving different methods to afford rigid and twisted molecules with high luminescence in solution and in the solid state have been reported in the literature.<sup>[5–10]</sup> The introduction of bulky substituents on the periphery, conjugation-induced rigidity, locking of the aromatic rings with heteroatoms, hydrogen bonding and metal ion complexation are some of the mised by using the PM6 method. When aggregates of the metallacycles were formed by adding hexane solutions in dichloromethane, aggregation-induced emission was observed for metallacycles **5** and **7**, and aggregation-caused quenching was observed for metallacycles **6** and **8**. The formation of aggregates was verified by dynamic light scattering and TEM analyses. Macrocycles **5** and **7** are white-light emitters in THF. Moreover, their high luminescence in both solution and the solid state was utilised for the recognition of nitroaromatic explosives.

strategies used to afford molecules with high luminescence in the solid state and in solution.  $^{\scriptscriptstyle [5-10]}$ 

Coordination-driven self-assembly is a potential approach to assemble desired building blocks in a specific pattern to obtain molecular architectures with desirable properties. The final assemblies inherit the physical and chemical characteristics of both the donors and acceptors.<sup>[11-18]</sup> Moreover, the selfassembled discrete molecules have the advantages of solution processability and stability. Several platinum(II) and palladium(II) fluorescent macrocycles and cages have been reported that showed solution-phase fluorescence behaviour.<sup>[12]</sup> However, their solid-state emission is less explored.<sup>[12d]</sup> It is proposed that incorporating an AIE-active ligand into a self-assembly will impart the molecule with both solution and solid-state emission. Recently, AIE-active platinum(II) assemblies were reported by the groups of Stang, Yang and Huang.<sup>[19]</sup> The assemblies exhibited solvent-dependent emission, dendrimer-dependent AIE and heparin-induced AIE. It is known that AIE-active molecules can display brilliant solid-state emissions, but none of the aforementioned assemblies were subjected to solid-state luminescence analysis.

To afford an AIE-active ligand, we focussed our attention on the 9,10-divinylanthracene moiety because its derivatives are highly luminescent in both solution and the solid state.<sup>[20]</sup> Different divinylanthracene derivatives have been used as mechanochromic materials, acid–base sensors, in spontaneous amplified emission and as charge-transport materials.<sup>[20]</sup> We decided to use 9,10-di(4-pyridylvinyl)anthracene (**3**) as the pyridyl donor for self-assembly (Scheme 1) with acceptors with suitable backbones. Carbazole and triphenylamine (TPA) derivatives have widely been applied as photosensitisers, charge–hole transport layers and emissive layers in organic light-emitting diodes (OLEDs), and AIE-active materials.<sup>[21–30]</sup> Hence, we de-

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Scheme 1. Self-assembly of molecular squares (5, 6) and hexagons (7, 8).

signed and synthesised two new diplatinum(II) organometallic acceptors **1** and **2** with carbazole and TPA backbones, respectively (see below).

We report herein the synthesis of a [4+4] and [6+6] self-assembled molecular square (5) and hexagon (7) upon treatment of linear donor **3** with Pt<sup>II</sup> acceptors **1** and **2**, respectively (Scheme 1). Two more analogous macrocycles (**6**, **8**) were synthesised by using donor 1,4-di(4-pyridylvinyl)benzene (**4**). The metallacycles **5** and **7** are fluorescent in solution and in the solid state and exhibit AIE activity. Their luminescence properties are influenced by solvent polarity and both **5** and **7** display white-light emission in THF. The luminescence of complexes **5** and **7** in both solution and the solid state was utilised for the detection of nitroaromatic compounds (NACs) in solution and in the vapour phase.

# **Results and Discussion**

# Synthesis and characterisation of 1 and 2

Carbazole-based Pt<sup>II</sup> acceptor **1** was prepared by means of the multi-step synthesis shown in Scheme 2. The ethynyl groups were introduced by Sonogashira coupling of  ${\bf b}$  with TMSA by using [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and Cul to afford c in 83% yield. Subsequent desilylation at room temperature in a mixture of dichloromethane and methanol (2:1) in the presence of K<sub>2</sub>CO<sub>3</sub> yielded d. Compound d was treated with trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>l<sub>2</sub>] in a mixture of diethylamine and toluene at room temperature with Cul to afford e. Compound e was treated with AqNO<sub>3</sub> in chloroform/MeOH (2:1) to obtain 1, which was triturated with diethyl ether to afford 1 as a grey solid in 80% yield. Dibromotriphenylamine (f) was prepared by following a procedure reported in the literature.<sup>[31]</sup> Compound **f** was converted into dialkyne (h) through Sonogashira coupling followed by desilylation of **q** in the presence of  $K_2CO_3$  at room temperature. The platinum-alkyne analogue (i) was synthesised in 57% yield by treating **h** with *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>] in the presence of Cul at



Scheme 2. Synthesis of the carbazole-based  $Pt^{\parallel}$  acceptor 1. NBS = *N*-bromosuccinimide, TMSA = trimethylsilylacetylene.

room temperature for 2 days. Treatment of i with AgNO<sub>3</sub> in a mixture of CHCl<sub>3</sub> and MeOH (2:1) for 24 h at room temperature afforded **2**. The crude product was washed with diethyl ether several times to obtain **2** as a yellow precipitate in 60% yield (Scheme 3).



**Scheme 3.** Synthesis of the TPA-based  $Pt^{\parallel}$  acceptor **2**.

The molecular structures of the iodide analogues **e** and **i** were established by single-crystal XRD analysis (Table 1). Suitable crystals of **e** and **i** were grown by slow evaporation of saturated solutions of the respective compounds in CHCl<sub>3</sub>. The phenyl ring at the carbazole nitrogen in **e** is twisted out of the plane of the fused ring system at an angle of 60.28° (Figure 1).

In the case of compound **i**, the unsubstituted phenyl ring of the TPA moiety is almost perpendicular to the other two phenyl rings at an angle of 84.40° (Figure 1).

#### Synthesis of self-assembled squares

The carbazole acceptor **1** was combined with both donors **3** and **4** separately in equimolar amounts. After heating the mixture of precursors **1** and **3** in acetone for 24 h, the colour of the solution changed from yellow to red. The solvent was re-



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Table 1. Crystallographic data and refinement parameters for ${\bf e}$ and ${\bf i}.^{^{[43]}}$					
	e	i			
formula	C <sub>46</sub> H <sub>71</sub> NP <sub>4</sub> I <sub>2</sub> Pt <sub>2</sub>	$C_{46}H_{73}NP_4I_2Pt_2$			
M <sub>w</sub>	1405.88	1407.89			
<i>T</i> [K]	298	298			
crystal system	triclinic	orthorhombic			
space group	ΡĪ	Fdd2			
a [Å]	15.2106(11)	32.493(3)			
<i>b</i> [Å]	18.4695(13)	37.744(3)			
c [Å]	20.6579(15)	8.5393(7)			
α [°]	100.930(2)	90			
β [°]	105.096(2)	90			
γ [°]	90.734(2)	90			
V [Å <sup>3</sup> ]	5489.7(7)	10472.7(15)			
Ζ	4	8			
$\rho_{\rm calcd}  [\rm g  \rm cm^{-3}]$	1.701	1.786			
$\mu(MO_{K\alpha})$ [mm <sup>-1</sup> ]	0.087	0.087			
λ [Å]	0.71073	0.71073			
F (000)	2704.0	6800.0			
no. of collected reflns	19319	59647			
no. of unique reflns	148738	5141			
goodness of fit (F <sup>2</sup> )	1.073	1.055			
R1 $[l > 2\sigma(l)]^{[a]}$	0.0539	0.0434			
$wR2[l > 2\sigma(l)]^{[b]}$	0.1414	0.0917			
[a] $R_1 = \Sigma  F_0  -  F_c  / \Sigma  F_0 $ . [b] wh	$R_2 = (\Sigma[w(F_0^2 - F_c^2] / \Sigma[w(F_0^2)^2]^{1/2}))$	2.			



Figure 1. Crystal structures of e (left) and i (right).

moved and the crude product was triturated with diethyl ether to afford a red solid (5) in high yield. The colour of the reaction mixture of 1 and 4 changed from light to deep yellow after heating for 24 h; a similar workup yielded 6 as a yellow solid. In the <sup>1</sup>H NMR spectrum of assembly 5, an upfield shift of acceptor protons was observed, which was expected to be due to coordination of the pyridyl nitrogen to the platinum(II) acceptor (Figure 2).



**Figure 2.** Partial <sup>1</sup>H NMR spectra of 1 and 5 in  $CDCI_3$  and a mixture of  $CDCI_3/$  [D.]MeOH (3:1), respectively.

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In the <sup>31</sup>P NMR spectrum, an upfield shift of about 8 ppm, with respect to the acceptor, was observed, which was consistent with the increase in electron density on the platinum(II) centre (Figure 3).

Although multinuclear NMR spectroscopy analysis indicated ligand to metal coordination and the formation of a single product in all cases, it did not provide any information about the compositions of the final assemblies. The compositions of **5** and **6** were determined by ESI-MS. In the ESI-MS spectrum, signals attributed to the fragments  $[5-4NO_3]^{4+}$  (m/z 1598.5459),  $[5-6NO_3]^{6+}$  (m/z 1045.0398) and  $[5-8NO_3]^{8+}$  (m/z 768.2763) were found. The signals were in good agreement with theoretical results and their isotopic distributions matched with the calculated values (Figure 4 and the Supporting Information). The formation of [4+4] self-assembled **6** was also confirmed by ESI-MS analysis (see the Supporting Information) in a similar way.

# Synthesis of self-assembled hexagons

The hexagons were obtained by equimolar self-assembly treatment of acceptor 2 with the corresponding donors. In the <sup>1</sup>H NMR spectrum of **7**, the TPA protons of the acceptor exhibited an upfield shift of about 0.1-0.14 ppm (see the Supporting Information). The <sup>31</sup>P NMR spectrum of **7** showed an upfield shift of around 4 ppm with respect to the free acceptor (2). The decrease in the coupling constant of the <sup>195</sup>Pt satellites (ca.  $\Delta J(Pt,P) = 202.80 \text{ Hz}$ ) is due to back donation of electrons from the ligand to the metal centre (Figure 5). Similar upfield shifts in the <sup>1</sup>H and <sup>31</sup>P NMR spectra of 8 were also observed (see the Supporting Information). The formation of [6+6] self-assembled hexagons (7 and 8) was established by the appearance of signals corresponding to the fragments  $[7-6NO_3]^{6+}$  (m/z)1600.5682),  $[7-8NO_3]^{8+}$  (*m*/*z* 1184.9825) and  $[8-8NO_3]^{8+}$  (*m*/*z* 1109.8880) in their respective mass spectra (see the Supporting Information).



**Figure 4.** Calculated (top) and experimental (bottom) isotopic distribution patterns of the signals corresponding to  $[5-6NO_3]^{6+}$  (*m/z* 1045.0398) and  $[5-8NO_3]^{8+}$ .



Figure 5.  $^{31}\text{P}$  NMR spectra of 2 and 7 in CDCl3 and CDCl3/[D4]MeOH (3:1) respectively.

#### Molecular modelling analysis

Several attempts to obtain suitable single crystals of the macrocycles were unsuccessful. Optimised geometries of the final assemblies were achieved by using the PM6 method (Figure 6). The optimised structure of square **5** is almost planar with phenyl rings of the carbazole moiety twisted out of the plane at an angle of  $55.3^{\circ}$ . The vinylanthracene moiety is twisted to reduce internal steric hindrance. The torsional angle between the anthracene moiety and adjacent pyridyl group is  $69.5^{\circ}$ . The width of the optimised structure of **5** was calculated to be 4 nm. Similarly, square **6** is also mostly planar with twisted carbazole rings and a divinylphenyl moiety with a width of 3.9 nm. The angle between the phenyl rings of the TPA acceptor in larger hexagon **7** was  $63.6^{\circ}$ . The hexagons **7** and **8** have large internal dimensions of  $6.7 \times 7.5$  nm and  $6.7 \times 7.4$  nm, respectively.

# Photophysical properties

In CH<sub>2</sub>Cl<sub>2</sub>, carbazole acceptor 1 exhibited two sets of absorption bands. Following previous reports in the literature, both bands in the  $\lambda = 240-260$  and 310-330 nm regions were ascribed to intramolecular  $\pi$ - $\pi$ \* transitions.<sup>[12]</sup> Acceptor **2** showed a single absorption band centred at  $\lambda = 360$  nm. Donor **3** exhibited two sets of absorption bands centred at  $\lambda = 230-260$  and 410 nm, which originated from  $\pi - \pi^*$  transitions.<sup>[12]</sup> Compound 4 had a single absorption band centred at  $\lambda = 350$  nm. Square **5** showed three absorption bands at  $\lambda =$  260, 320 and 425 nm, whereas **6** exhibited two absorption bands at  $\lambda = 260$  and 325 nm, along with a shoulder at  $\lambda = 420$  nm (see the Supporting Information). The major band at  $\lambda = 360$  nm, with a shoulder at  $\lambda = 435$  nm, was obtained for hexagon 7. All assemblies exhibited absorption bands of the acceptors and the donors (see the Supporting Information).

The assemblies have low solubility in hexane. Different hexane/ $CH_2Cl_2$  compositions were used to examine aggregate formation in solution. For all com-



Figure 6. Optimised structures of the macrocycles 5 (a), 6 (b), 7 (c) and 8 (d).

pounds, long-wavelength tails were observed due to scattering from spherical particles present in the medium (see the Supporting Information).<sup>[32]</sup> The formation of aggregates was further investigated by dynamic light scattering (DLS), SEM and TEM.

# AIE of 5 and 7

In self-assembled macrocycles, the rotational motion of the ligand is restricted by directional coordinate-bond formation. Therefore, the assemblies were highly emissive in solution. To investigate whether the final assemblies were AIE-active, the fluorescence spectra of the molecules were recorded with varying concentrations of hexane in CH<sub>2</sub>Cl<sub>2</sub> (Figure 7). Com-



**Figure 7.** Top: Change in fluorescence intensity of **5** with changing hexane/ CH<sub>2</sub>Cl<sub>2</sub> composition;  $\lambda_{ex}$ =425 nm. Bottom: images of **5** under  $\lambda$ =365 nm light in different solvent compositions.

pound **5** exhibited orange fluorescence with a peak maximum centred at  $\lambda = 556$  nm. When the hexane fraction slowly increased from 10 to 80%, the emission intensity gradually increased and became saturated. The gradual increase in fluorescence intensity of **5** with variation of the hexane fraction indicated that the molecule was AIE-active. In pure CH<sub>2</sub>Cl<sub>2</sub>, the quantum yield of **5** was measured to be 8.5%, but after aggregate formation the emission intensity increased and the final quantum yield was 21%. Analogous macrocycle **6** was excited at  $\lambda = 325$  nm and emission spectra with different hexane fractions were recorded (Figure 8).

On careful inspection, it was found that, with increasing hexane fraction, the emission intensity started to decrease; this is a general characteristic of ACQ. Therefore, two different types of fluorescence responses were observed from structurally similar macrocycles. Macrocycle **5**, which contains AIE-active donor **3**, exhibits AIE activity in solution, whereas macrocycle **6** 



Figure 8. Fluorescence intensity change with varying hexane/CH<sub>2</sub>Cl<sub>2</sub> fraction for 6;  $\lambda_{ex}$  = 350 nm.

shows ACQ upon aggregate formation. In discrete molecules (5 and 7), the motion of the donors was restricted by ligandto-metal bond formation, but a considerable amount of excitation energy was released in non-radiative decay pathways. When aggregated, the rotational motion of the donor molecules was completely arrested by the confined space, leading to the release of excitation energy only through the radiative decay pathway.<sup>[18,33]</sup> By changing the donor from a divinylphenyl analogue (4) to a divinylanthracene analogue (3), a change from ACQ to AIE behaviour was observed for structurally similar macrocycles.

#### DLS and microscopy analyses

To investigate the nature of the aggregates, DLS experiments were performed with all macrocycles in different solvent compositions. For a lower hexane fraction (60%), aggregates with an average diameter of 156 nm were formed in the medium. The size gradually increased to 190 nm with increasing hexane fraction (80%) and remained unchanged when more hexane was added (Figure 9). The spontaneous increase in aggregate size with variation of the hexane fraction proved that the emission intensity increased with increasing aggregate size. For compound **7**, the aggregate sizes gradually increased from 90 to 120 nm as the hexane fraction increased from 60 to 80%.

DLS provided evidence for the formation of spherical aggregates in the medium, but TEM analysis was performed to further explore the shape and size of the particles (Figure 10). For TEM analysis, appropriate solutions of the complex with different hexane/CH<sub>2</sub>Cl<sub>2</sub> compositions were drop-cast on copper grids and slowly dried to afford the final sample. For compound **5**, the average aggregate size increased from 150 to 190 nm as the hexane fraction changed from 60 to 80%. Changes in size with variation in solvent composition were also prominent for sample **7**; the sizes gradually changed from 90 to 120 nm with increasing hexane fraction. Two other mac-



**Figure 9.** Particle size distribution of the compounds with different hexane/ CH<sub>2</sub>Cl<sub>2</sub> compositions: 60 (a) and 80% hexane in CH<sub>2</sub>Cl<sub>2</sub> (b) for compound **5**; 60 (c) and 80% hexane in CH<sub>2</sub>Cl<sub>2</sub> (d) for compound **7**.

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Figure 10. TEM images of macrocycles with various hexane/CH<sub>2</sub>Cl<sub>2</sub> fractions. Compound 5 in 60 (a) and 80% hexane in CH<sub>2</sub>Cl<sub>2</sub> (b); compound 7 in 60 (c) and 80% hexane in CH<sub>2</sub>Cl<sub>2</sub> (d).

rocycles (**6** and **8**) also exhibited aggregate formation in different solvent mixtures (see the Supporting Information).

Finally, to explore the morphology of the aggregates, SEM was performed on aggregated samples deposited on carbon tape after drying. As observed in Figure 11, compound **5** retained the spherical morphology after drying, and the average sizes increased with increasing hexane fraction from 60 to 80%.



**Figure 11.** SEM images of the macrocycles with various hexane/ $CH_2CI_2$  fractions. Compound **5**: 60 (a) and 80% hexane in  $CH_2CI_2$  (b); compound **7**: 60 (c) and 80% hexane in  $CH_2CI_2$  (d).

Fluorescence studies in combination with DLS experiments and microscopy images confirmed that the emission enhancement in complexes **5** and **7** was due to aggregate formation.

#### Solvent-dependent fluorescence

The AIE behaviour of **5** and **7** prompted us to explore the role of different solvents on the photophysical properties. Non-

polar solvents, including toluene (Tol) and carbon tetrachloride, as well as polar solvents, such as  $CH_2CI_2$ , THF, Dioxane, DMSO and methanol (Figure 12) were chosen to investigate the role of solvents on the fluorescence of the compounds.



**Figure 12.** Top left: Solvent-dependent fluorescence of 5,  $\lambda_{ex} = 425$  nm. Top right: CIE diagram of 5. Bottom: images of 5 in different solvents under  $\lambda = 365$  nm UV light. Hex=hexanes, ACN=acetonitrile, Diox=Dioxane.

The emission intensity of **5** in non-polar solvents, such as  $CCl_4$  and Tol, was high, whereas in polar solvents, such as DMSO, methanol and ethyl acetate (EA), the intensity decreased (Figure 12). In non-polar solvents, the emission occurs from a locally excited (LE) state, but, when polar solvents were used, the LE state relaxed to a more stable and more polar state with lower energy. It is well known in the literature that the emission intensity from the polar state of fluorophores decreases due to different factors, including collisions with non-excited fluorophores and interactions with solvent molecules.

Upon careful inspection, the solution of **5** in THF was found to emit white light when excited at  $\lambda = 425$  nm. The chromaticity diagram (Figure 12, top right) shows that the solution in THF exhibits stable white-light emission (0.38, 0.43).<sup>[34]</sup> Compound **7** also exhibited similar white-light emission in THF (see the Supporting Information).

#### NAC detection

In recent years, cost-effective and rapid detection techniques for NACs have become an interesting field of research. Apart from being used as explosives, NACs are also valuable in the dye industry, in the manufacture of rocket fuel and in the pharmaceutical industry.<sup>[35]</sup> Due to high water solubility, NACs and the final explosive residues become sources of environmental pollution.<sup>[36]</sup>

Trinitrotoluene (TNT) is one of the oldest and most used NACs due to its abundance and explosive power. Several small molecules and polymer-based fluorescent sensors have been reported for the detection of TNT in solution.<sup>[37,38]</sup> For practical



applications, luminescent thin films that can detect explosive vapour are highly desirable. Several polyaromatic compounds, including anthracene, pyrene and TPA, have been used as electron-rich centres and anchoring templates for NACs in various self-assemblies.<sup>[39]</sup>

Although we are mainly interested in exploring compounds **5** and **7** for solid-state NACs detection, to get a preliminary idea on their possibility of sensing NACs, a fluorescence titration study with NACs was carried out in the solution phase.

Upon TNT addition, the emission intensity of **5** in solution gradually decreased. The addition of 4 equivalents of TNT quenched about 80% of the initial emission intensity of **5** (Figure 13).



Figure 13. Left: Fluorescence spectra of TNT titration with 5 in  $CH_2CI_2$  (left),  $\lambda_{ex}$  = 425 nm. Right: Stern–Volmer (SV) plot.

The SV constants were  $6.25 \times 10^3$  and  $1.54 \times 10^4 \, \text{m}^{-1}$  for **5** and **7**, respectively. The change in fluorescence lifetime of **5** and **7** upon the addition of TNT indicated dynamic quenching as the possible mechanism of quenching (Supporting Information).<sup>[40]</sup>

TNT and several other NACs, including 2,4-dinitrotoluene (DNT), 3,4-DNT, nitrotoluene (NT), trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), nitrobenzene (NB), nitromethane (NM), 3nitrobenzoic acid (NBA) and benzophenone (BPH), were treated with solutions of **5** and **7** to examine the selectivity. Of all the NACs, TNT showed maximum quenching efficiency (>80%), followed by DNT (>30%; see the Supporting Information). For compound **7**, except TNT and DNTs, other NACs did not show much change in fluorescence intensity. Therefore, both compounds were effective for the detection of TNT in solution.

For solid-state sensing, thin films of **5** and **7** were used; the films of **5** were exposed to saturated NB vapour and the change in fluorescence with time was monitored (Figure 14). After, 100 s of NB exposure, the initial emission intensity of **5** was quenched by 50%, and after 400 s of exposure a maximum of about 80% quenching was observed without any further quenching, even after longer exposure times. After 300 s of exposure towards saturated DNT vapour, the initial emission intensity of compound **5** was quenched by about 60%. For compound **7**, after 200 s, about 64% quenching of fluorescence was observed (see the Supporting information).

Solid-state quenching was attributed to a combined effect of the high vapour pressure of the analytes and their binding affinity towards the sensors. Thin films of compounds **5** and **7** 



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Figure 14. Titration of 5 with NB (top left) and 2,4-DNT (top right). Fluorescence images of thin films of compounds 5 and 7 after exposure to NB.

exhibited reversible sensing of NACs. After exposing the films to saturated NB vapour for a certain period of time, emission intensity was regained by washing the films with water followed by drying. The recovered film was reused for a certain number of times (Figure 15) with the retention of significant efficiency.



Figure 15. Fluorescence quenching efficiency versus number of cycles for 5.

The reusability of compound **7** was examined, and after five cycles of use a decrease in emission intensity was observed (see the Supporting Information). Therefore, both materials can be reused several times; this makes them potential candidates for in-field applications.

# Conclusion

We reported herein the synthesis of a pair of new platinum(II) ditopic acceptors with bite angles of  $90^{\circ}$  (1) and  $120^{\circ}$  (2), respectively. Self-assembly of these acceptors with linear dipyridyl donors with divinylanthracene (3) and divinylphenyl (4) backbones yielded molecular squares (5, 6) and hexagons (7, 8), respectively. Complexes 5 and 7 exhibited AIE behaviour that originated from the highly twisted bis(4-pyridyl)divinylan-



thracene donor (**3**). The role of the divinylanthracene backbone in the luminescence and AIE properties of these macrocycles (**5**, **7**) was illustrated by comparing the photophysical properties of a pair of analogous macrocycles (**6**, **8**), which showed ACQ luminescence. The formation of the aggregates was characterised by DLS, TEM and SEM analyses. The metallacycles (**5**, **7**) with a divinylanthracene backbone exhibited interesting solvent-dependent emissions, especially white-light emissions in THF; this makes them a rare class of coordination architectures for stable white-light emitters. Furthermore, thin films of the highly luminescent molecular square (**5**) and hexagon (**7**) showed efficient sensing of NAC explosives in the vapour phase through fluorescence quenching.

# **Experimental Section**

#### General

The starting materials and solvents were purchased from commercially available sources and used without further purification. Compounds 3, f, g, a and b were prepared according to procedures reported in the literature.<sup>[19,41]</sup> The NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer. The chemical shifts ( $\delta$ ) in the <sup>1</sup>H NMR spectra were reported in ppm relative to Me<sub>4</sub>Si as an internal standard ( $\delta = 0.0$  ppm) or the proton resonance resulting from incomplete deuteration of the NMR solvents:  $CDCl_3$  ( $\delta = 7.26$  ppm) and [D<sub>6</sub>]DMSO ( $\delta$  = 2.50 ppm). <sup>13</sup>C NMR spectra were recorded at 100 MHz, and the chemical shifts ( $\delta$ ) were reported in ppm relative to external CDCl<sub>3</sub> and [D<sub>6</sub>]DMSO at  $\delta =$  77.8–77.2 and 40.50 ppm, respectively. The <sup>31</sup>P NMR spectra were recorded at 120 MHz and the chemical shifts ( $\delta$ ) were reported in ppm relative to external 83% H<sub>3</sub>PO<sub>4</sub> at  $\delta = 0.0$  ppm. ESI-MS results were recorded by using an Agilent 6538 ultra-high definition (UHD) accurate mass Q-TOF spectrometer with standard spectroscopic-grade solvents. Electronic absorption and emission spectra were recorded on a Lambda 750 UV/Vis spectrophotometer and a Horiba Jobin Yvon Fluoromax-4 spectrometer. For the solid-state vapour exposure study, thin films of 5 and 7 were prepared by drop-casting and spin-coating of concentrated solutions on thin quartz films, which were vacuum dried for 6 h. Analytes (20 mg) were placed in a glass container and a cotton pad was placed on the sample to avoid direct contact with the sensor films. The containers were sealed with aluminium foil and kept for 2 days to generate saturated vapour. During the experiments, the thin films were placed on the cotton pad and after a certain period of exposure they were removed and immediately placed in the solid-state sample holder of the spectrofluorimeter. Single-crystal XRD data were collected with a Bruker D8 Quest diffractometer equipped with a Photon 100 detector with CMOS technology. The data were integrated by using SAINT and an empirical absorption correction was applied by SADABS. The structures were determined by direct methods by using SHELX-97.<sup>[42]</sup> Time-resolved fluorescence measurements were performed on an IBH-Data station platform by using a  $\lambda = 390$  nm nano-LED source. DLS experiments were performed on a zeta-sizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He–Ne laser ( $\lambda$  = 633 nm). Mixtures of CH<sub>2</sub>Cl<sub>2</sub>/hexane with various water fractions were prepared by slowly adding ultrapure hexane into solutions of the samples in CH<sub>2</sub>Cl<sub>2</sub>. SEM images were obtained by using a Zeiss Ultra-55 SEM instrument with the sample coated on a carbon tape. ESI mass spectra were recorded by using an Esquire 3000 plus ESI spectrometer. TEM analysis was performed on a JEOL 2100F instrument.

#### Synthesis of c

An oven-dried 100 mL two-necked round-bottomed flask was charged with **b** (1.00 g, 2.5 mmol), Cul (0.03 g, 8 mol%), triphenyl-phosphine (0.13 g, 20 mol%) and [Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub>] (0.08 g, 5 mol%). Freshly distilled triethylamine (50 mL) was added to the mixture, which was heated at 50 °C for 15 min. Trimethylsilylacetylene (0.65 g, 2.7 mmol) was added to the hot solution and the mixture was heated at reflux for 2 days. After completion of the reaction (as monitored by TLC), the solvent was removed and the compound was purified by column chromatography on silica gel (60:120) with CH<sub>2</sub>Cl<sub>2</sub>/hexane (5%) as the eluent to afford **c** as a yellow product (83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =8.25 (s, 2H), 7.62 (m, 2H), 7.51 (m, 5H), 7.28 (m, 2H), 0.30 ppm (s, 18H).

# Synthesis of d

A mixture of compound **c** (0.90 g, 2.06 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.35 g, 3.00 mmol) was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH (20:30) and stirred for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:4) as the eluent to give **d** as a yellow solid (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.27 (s, 2H), 7.62 (m, 2H), 7.54 (m, 5H), 7.31 (d, 2H), 3.10 ppm (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.8, 137.2, 131.0, 130.6, 128.7, 127.6, 125.2, 123.3, 121.3, 114.4, 110.6, 85.3, 76.2 ppm.

# Synthesis of e

Compound **d** (0.17 g, 0.60 mmol), *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (1.26 g, 1.81 mmol) and Cul (0.02 g, 0.06 mmol) were added to a freshly distilled mixture of toluene (30 mL) and diethylamine (15 mL) in a Schlenk flask. 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 product was purified by column chromatography with EA/hexane (1:1) as the eluent to afford **e** as a light-yellow solid (80 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.02 (s, 2 H), 7.61 (m, 5H), 7.53 (m, 2H), 7.34 (d, 2H), 2.29 (m, 24H), 1.22 ppm (m, 36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.7, 138.0, 130.3, 129.5, 127.9, 127.3, 123.5, 122.6, 120.7, 110.0, 101.2, 87.0, 17.1, 8.8 ppm; <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.63 ppm.

# Synthesis of 1

Compound **e** (0.05 g, 0.03 mmol) was dissolved in fresh CHCl<sub>3</sub> (7 mL) in a 20 mL vial. When the solution was treated with a solution of AgNO<sub>3</sub> (0.01 g, 0.07 mmol) in methanol (10 mL), a yellow precipitate started to form. The mixture was covered with aluminium foil and stirred in the dark at room temperature for 24 h. The solvent was completely dried and the crude product was filtered through Celite by using glass fibre and CHCl<sub>3</sub> as the solvent. Diethyl ether was added to induce the formation of an off-white precipitate, which was dried to afford the final product (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.95 (s, 2H), 7.62 (m, 2H), 7.51 (m, 3H), 7.28 (m, 4H), 2.03 (m, 24H), 1.28 ppm (m, 36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.9, 130.4, 129.9, 128.0, 127.3, 123.4, 122.9, 120.3, 110.0, 104.3, 15.0, 8.3 ppm; <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$  = = 20.07 ppm; IR:  $\tilde{\nu}$  = 2961(s), 2912 (m), 2105 (w), 1477 (s), 1266 (s), 1074 (s), 1016 (s), 779 cm<sup>-1</sup> (s).

#### Synthesis of h

CHCl<sub>3</sub> (30 mL) and MeOH (20 mL) were added to a mixture of  ${\bf g}$  (2.00 g, 4.56 mmol) and K\_2CO\_3 (2.5 g, 18.27 mmol) in a 100 mL

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round-bottomed flask, and the reaction mixture was stirred at room temperature for 24 h. The solvent was dried and the crude product was purified by column chromatography on silica gel (60:120) with EA/hexane (20%) as the eluent to give **h** (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.37$  (d, 4H), 7.29 (m, 2H), 7.11 (m, 3H), 7.01 (d, 4H), 3.05 ppm (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$  148.1, 147.0, 133.7, 130.1, 126.1, 125.6, 124.8, 123.7, 116.4, 84.1 ppm.

# Synthesis of i

Compound **h** (0.40 g, 1.36 mmol) and *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>l<sub>2</sub>] (2.85 g, 4.09 mmol) were dissolved in a freshly distilled mixture of toluene (30 mL) and diethylamine (15 mL) in a Schlenk flask. The flask was degassed under vacuum and refilled with nitrogen three times. Cul (0.02 g, 0.13 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. The solvent was removed under vacuum and the crude product was purified by column chromatography with EA/hexane (1:1) as the eluent to afford **i** as a light-yellow solid (57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =7.23 (d, 2H), 7.14 (d, 4H), 7.07 (d, 2H), 6.98 (d, 1H), 6.93 (d, 4H), 2.23 (m, 24H), 1.16 ppm (m, 36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =147.9, 145.6, 131.9, 129.6, 124.6, 124.2, 123.2, 123.1, 100.3, 88.8 ppm; <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$ =8.55 ppm.

# Synthesis of 2

Compound i (0.10 g, 0.07 mmol) was dissolved in a mixture of CHCl<sub>3</sub> (15 mL) and MeOH (10 mL). A yellow precipitate was formed upon the addition of AgNO<sub>3</sub> (0.03 g, 0.17 mmol) to the above mixture. The mixture was stirred for 24 h at room temperature in the dark. Upon completion, the solvents were removed and the product was extracted with chloroform. The product was isolated as a grey solid (60% yield) upon treating a concentrated solution in chloroform with diethyl ether. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.22 (m, 2H), 7.07 (m, 6H), 7.00 (m, 1H), 6.92 (d, 4H), 1.95 (m, 24H), 1.23 ppm (m, 36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.8, 145.9, 132.2, 129.7, 124.6, 124.1, 123.4, 122.7, 103.5, 65.8, 30.2, 14.9, 8.4 ppm; <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.03 ppm; IR:  $\tilde{\nu}$  = 2964 (m), 2932 (m), 2880 (m), 2105 (w), 1580 (m), 1471 (s), 1273 (s), 1023 (m), 984 (s), 824 (s), 734 cm<sup>-1</sup> (s).

#### General procedure for the synthesis of the macrocycles

To a stirred solution of the appropriate donor in acetone, a clear solution of the respective acceptor in acetone was added dropwise. The obtained reaction mixture was heated at reflux for 24 h. The volatile solvent was evaporated and the mixture was washed with cold diethyl ether and acetone to afford the desired final product.

# Synthesis of 5

Acceptor **1** (12.75 mg, 0.01 mmol) was treated with **3** (3.84 mg, 0.01 mmol) in acetone (5 mL) to afford the desired final product **5** (82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.60 (m, 16H), 8.49 (d, 8H), 8.25 (m, 16H), 7.93 (s, 8H), 8.87 (m, 16H), 7.48 (m, 24H), 7.43 (m, 16H), 7.21 (m, 12H), 6.94 (d, 8H), 1.83 (m, 96H), 1.18 ppm (m, 144H); <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$  = 16.02 ppm; IR:  $\bar{\nu}$  = 3450 (w), 2951 (m), 2111 (w), 1599 (s), 1471 (m), 1323 (s), 1260 9 s), 1086 (s), 1009(s), 818 (s), 734 cm<sup>-1</sup> (s); ESI-MS (*m/z*): 1598.5459 [**5**-4NO<sub>3</sub><sup>-</sup>]<sup>4+</sup>, 1045.0398 [**5**-6NO<sub>3</sub><sup>-</sup>]<sup>6+</sup>, 768.2763 [**5**-8NO<sub>3</sub><sup>-</sup>]<sup>8+</sup>.

#### Synthesis of 6

A solution of acceptor **1** (12.75 mg, 0.01 mmol) in acetone was added to a suspension of **4** (2.84 mg, 0.01 mmol) in acetone. After washing with cold diethyl ether and acetone, the product was obtained (86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.41 (m, 16H), 7.87 (s, 8H), 7.68 (d, 16H), 7.59 (s, 12H), 7.50 (m, 16H), 7.38 (m, 16H), 7.17 (m, 16H), 7.10 (d, 8H) 1.74 (m, 96H), 1.09 ppm (m, 144H); <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta$  = 16.01 ppm; IR:  $\tilde{\nu}$  = 3393 (m), 2970 (m), 2111 (w), 1587 9 s), 1458 (m), 1330 (s), 1023 (s), 798 (m), 753 cm<sup>-1</sup> (s); ESI-MS (*m/z*): 1186.5584 [**6**-5NO<sub>3</sub><sup>-</sup>]<sup>5+</sup>, 978.3634 [**6**-6NO<sub>3</sub><sup>-</sup>]<sup>6+</sup>.

# Synthesis of 7

A clear solution of **2** (12.78 mg, 0.01 mmol) in acetone was added to a suspension of **3** (3.84 mg, 0.01 mmol) in acetone (2 mL). After final purification, a red product was obtained (72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.46$  (s, 24 H), 8.39 (d, 12 H), 8.14 (m, 24 H), 7.69 (s, 24 H), 7.39 (m, 24 H), 7.08 (m, 18 H), 6.95 (m, 24 H), 6.90 (m, 24 H), 6.80 (m, 24 H), 1.70 (m, 144 H), 1.05 ppm (m, 216 H); <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>):  $\delta = 16.06$  ppm; IR:  $\tilde{\nu} = 3393$  (w), 2945 (m), 2105 (m), 1599 (s), 1497 (s), 1311 (s), 1247(s), 1093 (s), 1023 (s), 792 (s), 747 cm<sup>-1</sup> (s); ESI-MS (*m*/*z*): 1600.5682 [**7**-6NO<sub>3</sub><sup>-</sup>]<sup>6+</sup>, 1184.9825 [**7**-8NO<sub>3</sub><sup>-</sup>]<sup>8+</sup>.

# Synthesis of 8

Acceptor **2** (12.78 mg, 0.01 mmol) was treated with donor **4** (2.84 mg, 0.01 mmol) in acetone (5 mL) to afford the desired final product **5** (68%). <sup>1</sup>H NMR (CDCI<sub>3</sub>, 400 MHz):  $\delta$  = 8.34 (m, 24 H), 7.61 (m, 24 H), 7.54 (s, 24 H), 7.47 (d, 12 H), 7.09 (m, 18 H), 6.96 (m, 24 H), 6.92 (d, 24 H), 6.80 (m, 24 H), 1.69 (m, 144 H), 1.02 ppm (m, 216 H); <sup>31</sup>P NMR (120 MHz, CDCI<sub>3</sub>):  $\delta$  = 15.88 ppm; IR:  $\tilde{\nu}$  = 3406 (w), 2964 (m), 2111 (w), 1605 (m), 1497 (m), 1323 (m), 1266 (s), 1074 (s), 1016 (s), 792 cm<sup>-1</sup> (s); ESI-MS (*m/z*): 1109.8880 [**8**-8NO<sub>3</sub><sup>-1</sup><sup>8+</sup>.

# Synthesis of nanoaggregates

Stock solutions  $(10^{-3} \text{ M})$  of **5**, **6**, **7** and **8** were prepared by dissolving an appropriate amount of the complexes in spectroscopygrade CH<sub>2</sub>Cl<sub>2</sub>. Calculated amounts of aliquots from the stock solutions were transferred to a 4 mL glass vial and diluted with an appropriate amount of CH<sub>2</sub>Cl<sub>2</sub>. To generate aggregates, different amounts of hexane were added to the vials under vigorous stirring at room temperature to obtain solutions  $(10^{-5} \text{ M})$  with hexane fractions from 10 to 90%. The photophysical studies were carried out immediately because precipitates started to form if the solutions were kept for longer times.

# **DLS** measurements

For DLS analysis, solutions (2 mL) with varying hexane fractions were placed in a quartz cuvette with all transparent sides; the cuvette was placed in the instrument chamber for data collection. Each set of data was collected 10 times to obtain reproducible results.

# SEM analysis

For SEM analysis, carbon tapes of 1 mm<sup>2</sup> in size were placed in the SEM holder. Different solutions (10  $\mu$ L) of **5**, **6**, **7** and **8** in various solvent mixtures were drop-cast on the carbon tapes and the samples were air-dried overnight and then in vacuum for 6 h before data collection.

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#### **TEM analysis**

For TEM analysis, samples with different solvent compositions (60, 80 and 90% hexane) were chosen to explore the variation of aggregate sizes with changing hexane fractions in the system. Each sample (10  $\mu$ L) was drop-cast on copper grids and first air-dried overnight and then in vacuum before sample analysis.

#### Fluorescence quantum yield measurements

For fluorescence quantum yield measurements, quinine sulfate was chosen as a reference. The quantum yields were calculated by using Equation (1).

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

in which  $\phi_{\rm m}$  and  $\phi_{\rm r}$  are the radiative quantum yields of the compounds and reference, respectively;  $A_{\rm c}$  is the absorbance of the compound,  $A_{\rm r}$  is the absorbance of the reference;  $D_{\rm c}$  is the area of emission of the compound,  $D_{\rm r}$  is the area of emission of the reference, and  $N_{\rm c}$  and  $N_{\rm r}$  are the refractive indices of the compound and reference solutions, respectively.

#### Solvent-dependent fluorescence

For solvent-dependent fluorescence analysis, stock solutions  $(10^{-3} \text{ M}, 20 \text{ }\mu\text{L})$  of **5** and **7** were placed in 4 mL glass vials. The sample was diluted by the addition of different spectroscopy-grade solvents (1980  $\mu\text{L}$ ) to generate the final solution  $(10^{-5} \text{ m})$ .

#### NAC sensing

For fluorescence titration of the samples with NACs, a solution of **5/7** ( $10^{-5}$  M, 2 mL) was placed in a quartz cuvette. Fresh stock solutions of NACs in MeOH ( $10^{-3}$  M, 10 mL) were prepared. The NAC solutions were gradually added to the sensor solution.

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