## **Supplementary Materials for**

# Palladium(II) *N*-heterocyclic allenylidene complexes with extended intercationic Pd…Pd interactions and MMLCT phosphorescence

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#### **Experimental Section**

**Materials.** All starting materials were purchased from commercial sources and used as received. The solvents used for synthesis were of analytical grade unless stated otherwise. The solvents used for photophysical measurements were of HPLC grade. The compounds 2-ethynyl-1,3-dimethyl-1H-imidazol-3-ium hexafluorophosphate,  $[(C^N^N)PdCl]$  (HC^N^N = 6-phenyl-2,2'-bipyridine) and sodium 2,3,4tris(dodecyloxy)benzenesulfonate were prepared according to modified literature methods.<sup>1-5</sup>

Characterization. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P NMR spectra were recorded with Bruker Avance 400 FT-NMR and/or 500 FT-NMR spectrometers. Infrared spectra were recorded on a SHIMADZU IRTracer-100 spectrometer. UV-vis absorption spectra were recorded on a Thermo Scientific Evolution 201 UV-visible Spectrophotometer (all the absorption data were recorded in a one-cm cell, except the concentration dependent absorption spectra of 1a in CH<sub>3</sub>CN was recorded in a 2 mm cell). HR-MS (high resolution mass spectra) were obtained on a Thermo Scientific Q Exative mass spectrometer, operated in heated electrospray ionization (HESI) mode, coupled with Thermo Scientific Ultimate 3000 system. Photo-luminescent properties (solution and solid) were recorded via Edinburgh Spectrometer FLS-980 equipped with MCP-PMT dectetor. Emission lifetime measurements were performed with Hamamatsu compact fluorescence lifetime spectrometer C11367 and/or FLS-980 equipped with MCP-PMT detector with µF920H Xenon Flash lamp. Absolute luminescent quantum yields were recorded with Hamamatsu absolute PL quantum yield spectrometer C11347. Solidstate emissions at controlled variable temperature (77–373 K) were recorded with Oxford Instruments liquid nitrogen cryostat accessory. And fluidic emissions for variable temperature (20-80 °C) were recorded with thermoelectrically cooled fourwindow cuvette holder accessory. Emission, QY and lifetime for glassy solution(77 K) were recorded in butyronitrile.

Single crystals of **1a** (red needles) suitable for X-ray diffraction analysis were obtained by diffusion of diethyl ether into the DMF solution, while single crystals of **1a** (yellow blocks) were obtained by evaporation of the CH<sub>3</sub>CN solution. The

2

diffraction data were collected on a Bruker D8 Venture single crystal X-ray diffractometer. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXS or XT structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.

#### Synthesis and Characterization

Compounds 2-ethynyl-1,3-dimethyl-1H-imidazol-3-ium hexafluorophosphate, [(C^N^N)PdCl] (HC^N^N = 6-phenyl-2,2'-bipyridine) and sodium 2,3,4tris(dodecyloxy)benzenesulfonate were synthesized via literature methods with modifications.<sup>1-5</sup>

Synthesis of 2-ethynyl-1,3-dimethyl-1*H*-imidazol-3-ium hexafluorophosphate<sup>[1]</sup>

2-ethynyl-1,3-dimethyl-1H-imidazol-3-ium hexafluorophosphate



1-methyl-1H-imidazole (36.5 mmol, 3.0 g) was dissolved in THF (100 mL). "BuLi (2.5 M in hexane, 18 mL) was added dropwisely at -78 °C. After stirring for 2 h, the temperature was raised to -60 °C and I<sub>2</sub>(43.8 mmol, 11.12 g) in THF (40 mL) was added slowly. The mixture was stirring at RT for another 16 h and the reaction was quenched by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq, saturated). Organic phase was collected by extraction with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation under reduced pressure, the light yellow solid was collected. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and hexane gave pure 2-iodo-1-methyl-1H-imidazole (5.86 g, yield: 77%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  7.18 (d, *J* = 0.9 Hz, 1H), 6.98 (d, *J* = 0.9 Hz, 1H), 3.60 (s, 3H). 2-iodo-1-methyl-1*H*-imidazole (10 mmol, 2.32 g), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.5 mmol, 580 mg) and CuI (1 mmol, 190 mg) were dissolved in <sup>7</sup>Pr<sub>2</sub>NH (50 mL) under N<sub>2</sub>. After degassed ethynyltriisopropylsilane (12 mmol, 2.7 mL) was added, the reaction was kept stirring at RT for 48 h under N<sub>2</sub> atmosphere. The filtrate was collected and concentrated to dryness. EA was added and organic phase was washed with NaCl (aq, saturated) for 3 times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. EA was evaporated and 1-methyl-2-

((triisopropylsilyl)ethynyl)-1*H*-imidazole (1.78 g, yield: 68%) was gained as light yellow oil after column chromatography (SiO2, eluent: Hex : EA = 10 : 1). 1H NMR (400 MHz, CDCl3)  $\delta$  7.08 (d, *J* = 1.2 Hz, 1H), 6.97 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 1.14 (d, *J* = 4.0 Hz, 21H).

To a THF (5 mL) solution of 1-methyl-2-((triisopropylsilyl)ethynyl)-1*H*-imidazole (1 mmol, 262 mg), TBAF (2 mL, 1.0 mol/L in THF) was added. After the mixture was stirring at RT for 1 h, water (5 mL) was added and extracted with CH2Cl2 (20 mL). The organic phase was collected, washed with NaCl (aq, saturated) and dried over anhydrous Na2SO4. Light yellow oil collected after solvent was removed under reduced pressure at low temperature, was used directly by dissolving in CH2Cl2 (10 mL) at  $\Box$ 40 oC. After methyl trifluoromethanesulfonate (excess) was added, the reaction was kept at  $\Box$ 40 oC for 0.5 h. 2-ethynyl-1,3-dimethyl-1H-imidazol-3-ium triflate was collected by filtration as light brown solid (120 mg, yield: 45%), washed with few Et<sub>2</sub>O. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  7.43 (s, 2H), 4.75 (s, 1H), 3.87 (s,

6H). IR (KBr) 2126 cm<sup>-1</sup> (C=C). 2-ethynyl-1,3-dimethyl-1*H*-imidazol-3-ium hexafluorophosphate was obtained quantitatively by anion exchange with saturated NH<sub>4</sub>PF<sub>6</sub> aqueous solution and confirmed by <sup>19</sup>F and <sup>31</sup>P NMR. <sup>19</sup>F NMR (CD<sub>3</sub>CN, 376 MHz)  $\delta$ : –72.76; <sup>31</sup>P-NMR (CD<sub>3</sub>CN, 202 MHz)  $\delta$ : –144.62. The light brown solid collected was dried under vacuum and stored in the fridge.

### Synthesis of [(C^N^N)PdCl] (HC^N^N = 6-phenyl-2,2'-bipyridine)<sup>2-3</sup>

[(C^N^N)PdCl] (HC^N^N = 6-phenyl-2,2'-bipyridine)



Phenyllithium (36 mL, 1 M in Et<sub>2</sub>O) was added dropwise to 2,2'-bipyridine (30

mmol, 4.68 g) in 40 mL Et<sub>2</sub>O at 0 °C. The reaction was kept overnight while the temperature was raised to RT spontaneously. Then, the organic phase was extracted with Et<sub>2</sub>O after 50 mL was added to quench the reaction. The Et<sub>2</sub>O phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. After 70 mL acetone was added to dilute the sample, KMnO<sub>4</sub> (saturated in acetone) was added dropwise while stirring till the solution color remain slightly purple. The filtrate was purified by column chromatography (eluent: Et<sub>2</sub>O/Hexane = 2/7) to give a white solid. The crystalline pure target compound 6-phenyl-2,2'-bipyridine was obtained (1.5 g, yield: 22%). 1H NMR (400 MHz, CDCl3)  $\delta$  8.74 (d, *J* = 4.4 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 8.25–8.15 (m, 2H), 7.98–7.86 (m, 2H), 7.85–7.76 (m, 1H), 7.61–7.51 (m, 2H), 7.50–7.43 (m, 1H), 7.43–7.33 (m, 1H). 6-Phenyl-2,2'-bipyridine (2.11 mmol, 490 mg) and PdCl2(CH3CN)2 (2.11 mmol, 700 mg) were suspended in CH3CN (60 mL). The solution became clear when

temperature reached 80 oC. [(C^N^N)PdCl] (HC^N^N = 6-phenyl-2,2'-bipyridine) (320 mg, yield: 41%)

was collected as light yellow precipitate by filtration after refluxing overnight under N<sub>2</sub> balloon, washed with few CH<sub>3</sub>CN and Et<sub>2</sub>O subsequently and dried under vacuum. <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.65 (d, *J* = 4.5 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.26 (ddd, *J* = 12.2, 9.2, 4.7 Hz, 2H), 8.17 (t, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.2, 5.4 Hz, 1H), 7.65 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.53 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.10 (qd, *J* = 7.3, 3.5 Hz, 2H).

## Synthesis of sodium 2,3,4-tris(dodecyloxy)benzenesulfonate<sup>[4-5]</sup>

Na

sodium 2,3,4-tris(dodecyloxy)benzenesulfonate (NaLA)





$BrC_{12}H_{25}$	concentrated H <sub>2</sub> SO <sub>4</sub>
S. DIME, $R_2 C C_3$	

Pyrogallol (80 mmol, 10.1 g) and K<sub>2</sub>CO<sub>3</sub> were added to DMF (125 mL) and the

temperature was raised to 60 °C. Then  $BrC_{12}H_{25}$  (260 mmol, 62.4 mL) was added dropwise to the system and the reaction was kept stirring at 60 °C overnight. The mixture was cooled and poured into ice water and the precipitate was collected by filtration. Nearly quantitative yield of 1,2,3-tris(dodecyloxy)benzene was obtained as pale white solid after recrystallization from acetone. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 6.93 (t, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 2H), 3.98 (dt, *J* = 8.8, 6.6 Hz, 6H), 1.80 (ddd, *J* = 16.6, 14.6, 7.3 Hz, 6H), 1.53 –1.44 (m, 6H), 1.37 – 1.25 (m, 48H), 0.90 (t, *J* = 7.0 Hz, 9H).

Concentrated H<sub>2</sub>SO<sub>4</sub> (3 mL) was added to the 10 mL CHCl<sub>3</sub> solution of 1,2,3tris(dodecyloxy)benzene (1.6 mmol, 1.01 g). The reaction mixture heated at 40 °C for 15 min, then slowly poured into ice water. The pH of the solution was adjusted to 12 by adding NaOH (aq) with NaCl (aq). After stirring for 0.5 h, the reaction mixture was extracted with EA (50 mL) for three times. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated and purified by column chromatography (SiO<sub>2</sub>) with eluent EA and EtOH subsequently. The white solid (980 mg, yield: 84%) was obtained. <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.33 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 3.94 (dt, *J* = 8.4, 6.4 Hz, 4H), 3.83 (t, *J* = 6.4 Hz, 2H), 1.68 (dt, *J* = 14.5, 7.3 Hz, 6H), 1.48 – 1.38 (m, 6H), 1.25 (m, 48H), 0.85 (m, 9H).

Syntheses of Complexes 1a, 1b and 1c:



Scheme S1. Illustration of the synthetic procedure for complexes 1a, 1b and 1c

2-ethynyl-1,3-dimethyl-1*H*-imidazol-3-ium hexafluorophosphate (0.16 mmol, 44 mg) and Ag<sub>2</sub>O (0.2 mmol, 48 mg) were added to 15 mL CH<sub>3</sub>CN and the mixture was stirred under N<sub>2</sub> at RT overnight, protected from light. The light orange filtrate was collected after filtration through Celite. [(C^N^N)PdCl] (0.1 mmol, 37 mg) was then added to the solution. The reaction system was kept stirring under N<sub>2</sub> for another 12h at RT, protected from light. Filtrate collected after filtration through Celite was concentrated and dissolved in few CH<sub>3</sub>CN and precipitate with Et<sub>2</sub>O. The red solid **1a** (40 mg, yield: 66%) was obtained after filtration and column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>, eluent: CH<sub>3</sub>CN).

<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.62 (d, *J* = 5.0 Hz, 1H), 8.14 – 8.04 (m, 2H), 7.96 (t, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.48 (m, 1H), 7.18 (s, 2H), 7.12 – 7.04 (m, 2H), 3.83 (s, 6H); <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN)  $\delta$  163.23, 156.57, 154.22, 153.66, 151.50, 148.89, 147.84, 140.67, 140.21, 139.02, 132.21, 130.41, 127.52, 124.99, 124.92, 123.08, 120.95, 119.59, 119.25, 83.93, 35.47; <sup>19</sup>F NMR (CD<sub>3</sub>CN, 376 MHz)  $\delta$ : –72.67; <sup>31</sup>P-NMR (CD<sub>3</sub>CN, 202 MHz)  $\delta$ : –144.62; IR (KBr) 2104 cm<sup>-1</sup> (C=C=C); HR-MS (ESI): m/z = 457.06363, [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup>, calc. for [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup> m/z = 457.06391; HR-MS (ESI): m/z = 144.96343, [PF<sub>6</sub>]<sup>-</sup>, calc. for [PF<sub>6</sub>]<sup>-</sup> m/z = 144.96418. Complexes **1a** (40 mg) was suspended in MeOH (10 mL) at RT. Then, the excessive sulphate-type anion exchange resin was added slowly to the reaction system till the red suspension **1a** was totally dissolved. After 30 min stirring at RT, the filtrate was collected and concentrated to 0.5 mL. Red solid **1b** (20 mg, yield: 60%) was obtained after adding excessive Et<sub>2</sub>O and filtration.

<sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  8.71 (d, *J* = 5.1 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.16 (t, *J* = 7.8 Hz, 1H), 8.07–7.95 (m, 2H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.73–7.62 (m, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.44 (s, 2H), 7.17–7.02 (m, 2H), 3.96 (s, 6H); <sup>19</sup>F NMR (376 MHz, MeOD) no signal; <sup>31</sup>P NMR (202 MHz, MeOD) no signal; IR (KBr) 2100 cm<sup>-1</sup> (C=C=C); HR-MS (ESI): m/z = 457.06378, [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup>, calc. for [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup> m/z = 457.06391.

Complexes 1a (0.04 mmol, 24 mg) in CH<sub>3</sub>CN (5 mL) and sodium 2,3,4-

tris(dodecyloxy)benzenesulfonate (0.039 mmol, 29 mg) in  $CH_2Cl_2$  (5 mL) were mixed at RT, and kept stirring for 2 h after adding 4 mL H<sub>2</sub>O. The organic layer was collected and washed with H<sub>2</sub>O several times. The solvent was evaporated to give a yellow solid. The final target yellow complex **1c** (40 mg, yield: 86%) was obtained after recrystallization in hot DMSO.

<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.77 (s, 1H), 8.55 (s, 1H), 8.37 – 8.17 (m, 3H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.84–7.67 (m, 3H), 7.63 (s, 2H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.15 (s, 2H), 6.63 (d, *J* = 8.6 Hz, 1H), 4.18–3.70 (m, 12H), 1.68 (m, 6H), 1.34 (m, 48H), 0.86 (m, 9H). <sup>19</sup>F NMR (376 MHz, DMSO) no signal; <sup>31</sup>P NMR (202 MHz, DMSO) no signal; IR (KBr) 2102 cm<sup>-1</sup> (C=C=C); HR-MS (ESI): m/z = 457.06383, [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup>, calc. for [C<sub>23</sub>H<sub>19</sub>N<sub>4</sub>Pd]<sup>+</sup> m/z = 457.06391; HR-MS (ESI): m/z = 709.54425, [C<sub>42</sub>H<sub>77</sub>O<sub>6</sub>S]<sup>-</sup>, calc. for [C<sub>42</sub>H<sub>77</sub>O<sub>6</sub>S]<sup>-</sup> m/z = 709.54463.

	1a (yellow block)	1a DMF (red needle)
formula	$C_{23} H_{19} F_6 N_4 P P d$	C <sub>26</sub> H <sub>26</sub> F <sub>6</sub> N <sub>5</sub> O P Pd
fw	602.79	675.89
color	yellow	red
crystal size (mm)	$0.40 \times 0.32 \times 0.28$	$0.32 \times 0.04 \times 0.03$
crystal system	<i>P</i> -1	<i>P</i> -1
space group	trinclinic	trinclinic
<i>a</i> , Å	8.2664(11)	6.5861(5)
b, Å	11.9680(15)	12.6581(10)
<i>c</i> , Å	12.4012(16)	17.1310(14)
α, deg	73.332(4)	109.005(3)
$\beta$ , deg	73.511(4)	99.386(3)
γ, deg	74.085(4)	92.908(4)
<i>V</i> , Å <sup>3</sup>	1101.9(2)	1323.96(18)
Ζ	2	2
$D_{\rm c}$ , g cm <sup>-3</sup>	1.817	1.695
$\mu$ , mm <sup>-1</sup>	0.986	6.887
<i>F</i> (000)	600	680.0
$2\theta_{\rm max}$ , deg	27.533	65.356
no. reflections	11570	4324
no. independent	$5010 [R_{int} = 0.0596]$	4324 [R <sub>int</sub> = 0.0639]
reflections		
no. variables	319	344
$GOF$ on $F^2$	1.035	0.992
$R_1^a$	0.0314	0.0999
$wR_2^{b}$	0.0799	0.2670
residual $ ho$ , eÅ <sup>-3</sup>	+0.693, -0.525	+1.550, -1.439

 Table S1. Crystal Data for 1a (both yellow block like and red needle form)

 $\frac{1}{a R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ b Rw} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]\}^{1/2}.$ 

Complex	Medium	$\lambda_{\rm rbs}/\rm nm$	$\lambda_{\rm m}/\rm nm(\tau/\rm us)$	Ф
complex	Weatum	( ( 103 1-11 3 -1))	$\chi_{em}/\min(t/\mu s)$	Ψem
		$(\varepsilon / \times 10^{5} \text{ mol}^{-1} \text{dm}^{3} \text{cm}^{-1})$		
1a	CH <sub>3</sub> CN (298 K) (10 <sup>-5</sup> M)	264 (35.9), 280 (39.8), 319	Non-emissive	
		(18.8), 333 (15.2)		
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN (77 K)		570 (13.0)	>99%
	(1.6×10 <sup>-4</sup> M)			
	Solid (298 K) (red powder)		695 <sup><i>a</i></sup> (1.2)	43%
1b	MeOH (298 K) (10 <sup>-5</sup> M)	266 (29.4), 278 (32.1), 319	Non-emissive	
		(14.6), 335 (11.3)		
	H <sub>2</sub> O (298 K) (10 <sup>-5</sup> M)	276 (22.1), 311 (10.5)	625 (0.32)	4%
	Solid (298 K) (red powder)		655 (0.27)	29%
1c	CH <sub>2</sub> Cl <sub>2</sub> (298 K) (10 <sup>-5</sup> M)	269 (33.3), 281 (35.4), 320	Non-emissive	
		(16.4), 337 (12.6)		
	Toluene (298 K) (10-5 M)	291 (14.1), 332 (8.9), 346 (9.7),	610 (0.26)	14%
		528 (3.7)		
	Solid (298 K (yellow		550 (0.48)	14%
	powder)			
	Solid (298 K) (red powder)		630 (0.45)	46%

#### **Table S2.** Photophysical Data.

<sup>*a*</sup> The solid-state emission data of **1a** illustrated here is the one with the emission peak maximum at longest wavelength ever measured (consistence with the spectra show in Figure S13). As the emission spectra of **1a** is strongly dependent of the Pd…Pd interactions, the emission spectra varies from time to time, depending on the subtle variations for post-treating and measuring conditions, which may result in the alteration of the Pd…Pd distances.

## NMR spectra

## **Complex 1a**



Figure S1. <sup>1</sup>H-NMR spectrum of 1a in CD<sub>3</sub>CN (500 MHz)



Figure S2. <sup>13</sup>C-NMR spectrum of 1a in CD<sub>3</sub>CN (126 MHz).



Figure S3. <sup>19</sup>F-NMR spectrum of 1a in CD<sub>3</sub>CN (376 MHz).



50 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -50 -100 -120 -140 -160 -180 -200 -220 -220 -240 fil (span)

Figure S4. <sup>31</sup>P-NMR spectrum of 1a in CD<sub>3</sub>CN (202 MHz).



Figure S5. H-H COSY (CD<sub>3</sub>CN, 500 MHz) spectrum of 1a (0.10 mg/mL) at RT.



Figure S6. Concentration dependent <sup>1</sup>H-NMR spectra of 1a in CD<sub>3</sub>CN (500 MHz).

## **Complex 1b**



Figure S7. <sup>1</sup>H-NMR spectrum of complex 1b in MeOD (500 MHz).



Figure S8. <sup>1</sup>H-NMR spectrum of complex 1c in DMSO (400 MHz).

## HR-MS (ESI) spectra:



**Figure S9.** The HR-MS (ESI) spectra of **1a** with positive mode (a) and negative mode (b) respectively.



Figure S10. The HR-MS (ESI) spectra of 1b with positive mode



**Figure S11**. The HR-MS (ESI) spectra of **1c** with positive mode (a) and negative mode (b) respectively.



Absorption and emission spectra

**Figure S12.** Electronic absorption spectra of complexes **1a** ( $10^{-5}$  M in CH<sub>3</sub>CN), **1b** ( $10^{-5}$  M in MeOH and H<sub>2</sub>O) and **1c** ( $10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub> and toluene) at 298 K.



**Figure S13.** Solid-state excitation and emission spectra of **1a** (red powder), **1b** (red powder) and **1c** (yellow powder and grinded red powder) at RT. (*Note*: the solid-state emission spectra of **1a** shown here is the one with the emission peak maximum at longest wavelength ever measured, which is consistence with the photophysical data list in Table S2.)





**Figure S14**. Normalized solid-state emission (excitation @ 400 nm) spectra changes of complex **1a** at variable temperatures (77–377 K), starting from red powder in ambient conditions.



Figure S15. Excitation (emission @ 630 nm) and emission spectra (excitation @ 420 nm) of complex 1a with various concentrations in CH<sub>3</sub>CN at RT.



**Figure S16**. Concentration dependent emission of complex **1a** (excitation @ 450 nm) in CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN at 77 K (glassy solution).

## **Complex 1b**



Figure S17. Excitation (emission @ 625 nm) and emission spectra (excitation @ 365 nm) of complex 1b with various concentrations in  $H_2O$  at RT.

## **Complex 1c**



**Figure S18.** Optical micrographs of complex **1c** between two crossed polarizers before and after grinding at RT. The double arrows indicate the configurations of the polarizers.



**Figure S19**. Temperature-dependent excitation (emission @ 609 nm) and emission (excitation @ isosbestic point 345 nm) spectra of complex **1c**.

#### Supramolecular aggregation model analysis for complex 1c in toluene

The isodesmic self-association model assumes that monomers aggregate in an one dimensional, noncyclic manner.<sup>6,7</sup> The reversible formation of noncovalent bonds is identical for all binding, in which the equilibrium constants and Gibbs free energy changes are equal for each step of the aggregation process. The cooperative nucleation-elongation model describes the equilibrium between the monomer pool and supramolecular polymers (oligomer nucleus formation), and the cooperative growth of the latter,<sup>7-10</sup> in which the process can be separated into a nucleation and an elongation phase.

The temperature-dependent isodesmic self-assembly model can be described by the function as:

$$\alpha_{agg}(T) \cong \frac{1}{1 + \exp\left(-0.908\Delta H \frac{T - T_m}{RT_m^2}\right)}$$
(1)

Whereas,  $\Delta H$  is enthalpy corresponding to the aggregation process and  $T_m$  is the melting temperature.

The temperature-dependent nucleation-elongation self-assembly model can be described by the functions in two regimes:

Nucleation regime:

$$\alpha_{agg} = \sqrt[3]{K_a} \exp\left[\left(\frac{2}{3\sqrt[3]{K_a}} 1\right) \left| \frac{\Delta H_e}{RT_e^2} (T - T_e) \right]\right]$$
(2)

Elongation regime:

$$\alpha_{agg} = \alpha_{sat} \left[ \left[ 1 - \exp \left[ \frac{-\Delta H_e}{RT_e} \left( T - T_e \right) \right] \right] \right]$$
(3)

$$\langle N_n \rangle = \frac{1}{\sqrt{K_a}} \sqrt{\frac{\alpha_{agg}}{\alpha_{sat} - \alpha_{agg}}}$$
 (4)

$$\left\langle N_n\left(T_e\right)\right\rangle = \frac{1}{\sqrt[3]{K_a}} \tag{5}$$

Whereas,  $\Delta H_e$  is enthalpy corresponding to the aggregation (elongation) process;  $T_e$  is elongation temperature;  $\alpha_{sat}$  is parameter introduced in the equation to ensure that  $\alpha_{agg}/\alpha_{sat}$  does not exceed unity;  $K_a$  is dimensionless equilibrium constant of the activation step at the elongation temperature;  $\langle N_n \rangle$  is the number-averaged degree of polymerization in the elongation regime, averaged over all active species.

According to the fitting results with both cooperative nucleation-elongation and isodesmic models, the data ( $\lambda = 528$  nm) for the degree of aggregation against temperature imply the aggregation process of **1c** prefers the cooperative model (Figure S20-22).



Figure S20. Degree of aggregation for complex 1c as a function of the temperature, obtained by fitting the absorbance at the distinct band ( $\lambda = 528$  nm) to the isodesmic model.



Figure S21. Degree of aggregation for complex 1c as a function of the temperature, obtained by fitting the absorbance at the distinct band ( $\lambda = 528$  nm) to the nucleation-elongation (cooperative) model.



**Figure S22**. Fitting of degree of aggregation against temperature ( $\lambda = 528$  nm) in the framework of the cooperative nucleation–elongation and isodesmic models.

**Table S3**. Thermodynamic parameters  $\Delta H_e$ ,  $T_e$ ,  $K_a$ , and  $\langle N_n(T_e) \rangle$  obtained from the temperature-dependent UV-Vis experiments of **1c** in toluene on the basis of the nucleation-elongation model developed by Meijer, Schenning and Van der Schoot model.<sup>7-9</sup>

Conc. / M	$\alpha_{sat}$	$\Delta H_e / \text{kJ mol}^{-1}$	<i>T</i> <sub>e</sub> / K	$K_a$ / $M^{-1}$	$< N_n(T_e) >$
1×10 <sup>-5</sup>	1.153	-46.9	336.2	7.9×10 <sup>-4</sup>	10.8

### **Computational Results**

All calculations were performed with Gaussian09 suite of program<sup>11</sup> employing density functional theory (DFT) and time-dependent density functional theory (TDDFT). Fully geometry optimization of ground state and the lowest triplet excited state (T1) were carried out for monomeric and dimeric Pd(II) NHA cations. Functional B3LYP<sup>12</sup> with the third generation dispersion correction (D3)<sup>13</sup> was applied. The effective core potentials (ECPs) and its accompany basis set LanL2DZ<sup>14,15</sup> was employed for Pd atom, the 6-31G(d)<sup>16</sup> basis set was employed for other atoms. Frequency calculations were performed at the same theoretical level to verify the correct stationary points. TDDFT calculations were done based on the fully optimized ground state structure to obtain the energy of vertical electronic excitation and the corresponding oscillator strength. The solvent effects have been studied using self-consistent reaction field (SCRF) method based on PCM models<sup>17,18</sup> with toluene as solvent based on the solvent media for experiments.

	Wavelength / nm	Oscillator Strength	Transition configuration	CI coeff
Monomer	414.9	0.003	H→L	0.69
	385.2	0.010	H-2→L	0.60
			H-1→L	0.35
	368.2	0.108	H-1→L	0.60
			H-2→L	0.34
	344.0	0.099	H-3→L	0.65
			H-2→L	0.13
	330.2	0.172	H-3→L	0.53
			H→L+1	0.34
Dimer	489.4	0.047	H→L	0.70
	389.9	0.020	$H \rightarrow L+3$	0.46
			H-1→L+1	0.46
	388.0	0.024	$H \rightarrow L+3$	0.53
			H-1→L+1	0.42
	369.7	0.129	H <b>-</b> 3→L+1	0.59
			H-4→L	0.33
	341.0	0.186	$H\rightarrow L+5$	0.47
			H→L+9	0.29

**Table S4.** Calculated absorption properties of monomeric and dimeric Pd(II) NHA cation in toluene.



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Figure S23. Calculated MOs of monomeric and dimeric Pd(II) NHA cations in toluene.



**Figure S24.** Calculated frontier MO energy levels of monomeric and dimeric Pd(II) NHA cations in toluene.



Figure S25. Fully optimized geometry of the dimer in ground state and T1 state in toluene.

	Wavelength / nm	Oscillator Strength	Transition configuration	CI coeff
Monomer	463.8	0.003	H→L	0.70
	416.0	0.003	H-2→L	0.69
			H-1→L	0.11
	386.6	0.068	H-1→L	0.67
			H-3→L	0.15
	347.0	0.050	$H \rightarrow L+1$	0.66
			H-3→L	0.13
	330.9	0.110	$H \rightarrow L+2$	0.63
			H-3→L	0.21
Dimer	506.3	0.029	H→L	0.70
	376.8	0.057	H-4→L	0.66
			$H \rightarrow L+3$	0.16
	372.4	0.016	H-3→L+1	0.65
			H-6→L	0.15
	350.3	0.070	H-1→L+2	0.39
			H <b>-</b> 6→L+1	0.33
			H-5→L	0.30
	348.0	0.034	H-7→L	0.43
			H-5→L+1	0.36

**Table S5.** Calculated absorption properties of monomeric and dimeric Pd(II) NHA cation based on crystal structures.



**Figure S26.** Calculated MOs of monomeric and dimeric Pd(II) NHA cations based on crystal structure.

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