Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information (ESI)

Photo-Modulated Supramolecular Self-Assembly of ortho-Nitrobenzyl Ester-BasedAlkynylplatinum(II)2,6-Bis(N-alkylbenzimidazol-2'-yl)pyridineComplexes

Andy Shun-Hoi Cheung, Michael Ho-Yeung Chan, Charlotte Po, Eugene Yau-Hin Hong and Vivian Wing-Wah Yam*

Institute of Molecular Functional Materials and Department of Chemistry,

The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

* Corresponding author: wwyam@hku.hk

Experimental

Materials and Reagents

Dimethyl sulfoxide (DMSO) was purchased from Acros Organics. Chloroform-d and dimethyl sulfoxide- d_6 were purchased from Cambridge Isotope Laboratories, Inc. Tetra-n-butylammonium fluoride solution (1.0 M in THF) was purchased from J & K Scientific Ltd. Methyl 2-iodobenzoate was purchased from Sigma-Aldrich Chemcial Co. 2-Nitrobenzyl 4-ethynylbenzoate,¹ 4-ethynyl benzoic acid² and 2-ethynyl benzoic acid² were synthesized and purified according to reported procedures. All other commercially available reagents were of analytical grade and were used as received. All solvents were purified by the Innovative Technology, Inc. PureSolv MD 5 Solvent Purification System before use. All amines were distilled over sodium hydroxide and stored over sodium hydroxide before use. All reactions were performed under inert and anhydrous conditions using standard Schlenk techniques unless specified otherwise.

Physical Measurements and Instrumentation

¹H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) NMR spectrometers with chemical shifts relative to tetramethylsilane (Me₄Si). Electron impact (EI) mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. High-resolution electrospray ionization (ESI) mass spectra were recorded on a Bruker maXis II high-resolution QTOF mass spectrometer. All elemental analyses were performed on a Flash EA 1112 elemental analyser by the Institute of Chemistry at the Chinese Academy of Sciences in Beijing. UV-Vis absorption spectra were obtained by using a Varian Cary 50 UV/Vis spectrophotometer. Emission spectra were recorded on an Edinburgh Instrument FS5 spectrofluorometer. Diffractometer in Bragg-Brentano ($\theta/2\theta$) reflection mode with a graphite monochromatized Cu-K_a radiation ($\lambda = 1.54178$ Å) and nickel filter. Photoirradiation was performed using a 300 W Oriel Corporation model 60011 Xe (ozone-free) lamp, and monochromatic light was obtained by passing the light through an Applied Photophysics F3.4 monochromator. The UV-vis spectral changes upon UV irradiation was monitored by an Agilent Cary 8454 diode array spectrophotometer. Transmission electron microscopy (TEM) experiments were performed on a Philips CM100 transmission electron microscope. The selected area electron diffraction (SAED) experiments were performed on a FEI Tecnai G2 20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. All carbon-coated copper grids were pre-treated with a PELCO easiGlow Glow Discharge Cleaning System. Samples were prepared by dropping a few drops of sample solution onto the grids and dried by slow evaporation of the solvents. Dynamic light scattering (DLS) experiments were conducted at 298 K using a Malvern (UK) Zetasizer ZS90 with internal HeNe laser (λ_0 = 632.8 nm).

Determination of the conversion of 1a upon UV irradiation

The conversion of **1a** into its uncaged product has been monitored by ¹H NMR spectroscopy before and after UV irradiation for about 20 hours. The cleavage of the *o*-NB ester group would lead to loss of protons in the $[-CH_2-C_6H_4-NO_2]$ moiety. Therefore, the peaks corresponding to the $[-CH_2-C_6H_4-NO_2]$ moiety have been monitored. By calibrating the integral of the terminal $-CH_3$ group as 6, the integrals of the protons in the $[-CH_2-C_6H_4-NO_2]$ moiety are determined to be 1.95 and 1.67 before and after UV irradiation respectively, which corresponds to the 14.4 % conversion. In parallel to the calibration by the terminal methyl group, the integrals of the protons in the $[-CH_2-C_6H_4-NO_2]$ moiety are also calibrated by the integrals of the protons in the pyridine moiety on the bzimpy ligand. By comparing the corresponding integrals in the $[-CH_2-C_6H_4-NO_2]$ moiety, the decrease in the integral is determined to be 17.8 %. Based on these calculations, the proportion of complexes undergoing photolysis is determined to be 16.1 %.

Synthetic Procedures

2-Nitrobenzyl 2-iodobenzoate. It was prepared according to a modification of the procedure reported for the synthesis of 4,5-dimethoxy-2-nitrobenzyl 4-iodobenzoate,¹ except that 2-iodobenzoic acid (3.01 g, 12.1 mmol) was used in place of 4-iodobenzoic acid. Yield: 3.72 g, 9.71 mmol; 80.2 %. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to SiMe₄, δ /ppm): δ 5.79 (s, 2H, –OCH₂–), 7.16–7.22 (m, 1H, phenyl), 7.41–7.55 (m, 2H, phenyl), 7.65–7.73 (m, 2H, phenyl), 7.86 (d, *J* = 8.0 Hz, 1H, phenyl), 8.02 (d, *J* = 8.0 Hz, 1H, phenyl), 8.13 (d, *J* = 8.0 Hz, 1H, phenyl). HRMS (Positive ESI): calcd for C₁₄H₁₀INO₄, *m*/z 383.9727; found: 383.9674 [M+H]⁺.

2-Nitrobenzyl 2-((trimethylsilyl)ethynyl)benzoate. It was prepared according to a modification of the procedure reported for the synthesis of 4,5-dimethoxy-2-nitrobenzyl 4-((trimethylsilyl)ethynyl)benzoate,¹ except that 2-nitrobenzyl 2-iodobenzoate (3.02 g, 7.88 mmol) was used in place of 4,5-dimethoxy-2-nitrobenzyl 4-iodobenzoate Yield: 3.21 g, 7.34 mmol; 93.1 %. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to SiMe₄, δ /ppm): δ 0.19 (s, 9H, -Si(CH₃)₃), 5.81 (s, 2H, -OCH₂-), 7.38-7.42 (m, 1H, phenyl), 7.47-7.51 (m, 2H, phenyl), 7.62-7.67 (m, 2H, phenyl), 7.79 (d, *J* = 7.7 Hz, 1H, phenyl), 7.96 (d, *J* = 7.7 Hz, 1H, phenyl), 8.14 (d, *J* = 7.7 Hz, 1H, phenyl). HRMS (Positive EI): calcd for C₁₉H₁₉O₄NSi, *m*/z 353.1078; found: 353.1086 [M]⁺.

2-Nitrobenzyl 2-ethynylbenzoate. It was prepared according to a modification of the procedure reported for the synthesis of 4,5-dimethoxy-2-nitrobenzyl 4ethynylbenzoate,¹ except that 2-nitrobenzyl 2-((trimethylsilyl)ethynyl)benzoate (2.04 g, 4.66 4,5-dimethoxy-2-nitrobenzyl 4mmol) was used in place of ((trimethylsilyl)ethynyl)benzoate. Yield: 1.22 g, 4.34 mmol; 93.1 %. ¹H NMR (400

MHz, CDCl₃, 298 K, relative to SiMe₄, δ /ppm): δ 3.36 (s, 1H, $-C\equiv$ CH), 5.81 (s, 2H, $-OCH_2-$), 7.42–7.55 (m, 3H, phenyl), 7.64–7.69 (m, 2H, phenyl), 7.75–7.77 (m, 1H, phenyl), 8.01 (d, J = 8.2 Hz, 1H, phenyl), 8.13 (d, J = 8.2 Hz, 1H, phenyl). HRMS (Positive ESI): calcd for C₁₆H₁₁NaNO₄, m/z 304.0580; found: 304.0580 [M+Na]⁺.

General synthetic procedures of complexes 1a–2b. The complexes were prepared according to a modification of the reported procedures for the related alkynylplatinum(II) bzimpy complexes.^{3,4} To a stirred solution of the corresponding chloroplatinum(II) bzimpy precursors and the respective alkyne in dimethylformamide or dichloromethane was added a catalytic amount of copper(I) iodide and triethylamine. After removal of solvent, the crude product was purified either by column chromatography using chloroform as the eluent or by slow diffusion of diethyl ether vapor into the concentrated dimethylformamide solution to give the products as yellow or orange solids.

[Pt{bzimpy(C₁₀H₂₁)₂}{C=C-C₆H₄-(COOCH₂-C₆H₄-NO₂-2)-4}]PF₆ (1a). This was synthesized from [Pt(R₂-Bzimpy)Cl]PF₆ (R = C₁₀H₂₁) (150 mg, 0.155 mmol) and 2-nitrobenzyl 4-ethynylbenzoate (63.2 mg, 0.225 mmol). Complex 1a was obtained as an orange solid. Yield: 75.1 mg, 0.0620 mmol; 40.0 %. ¹H NMR (400 MHz, [D₆]-DMSO, 298 K, relative to SiMe₄, δ /ppm): δ 0.79–0.82 (m, 6H, –CH₃), 1.16–1.18 (m, 24H, –CH₂-), 1.32–1.34 (m, 4H, –CH₂-), 1.77–1.80 (m, 4H, –CH₂-), 4.60–4.63 (m, 4H, –N–CH₂-), 5.71 (s, 2H, –OCH₂-), 7.50–7.60 (m, 6H, phenyl and benzimidazolyl), 7.69–7.70 (m, 1H, phenyl), 7.79–7.86 (m, 4H, benzimidazolyl), 8.08–8.10 (m, 2H, benzimidazolyl) 8.17–8.26 (m, 3H, phenyl), 8.38–8.45 (m, 3H, pyridine). HRMS (Positive ESI): calcd for C₅₅H₆₃N₆O₄Pt, *m*/*z* 1066.4557; found: 1066.4551 [M–PF₆]⁺. Elemental analysis calcd (%) for C₅₅H₆₃F₆N₆O₄Pt•0.5CHCl₃: C, 52.41; H, 5.03; N,

6.61; found: C, 52.53; H, 4.94; N, 6.50.

[Pt{bzimpy(C10H21)2}{C=C-C6H4-(COOH)-4}]PF6 (1b). This was synthesized from [Pt(R2-Bzimpy)Cl]PF6 (R = C10H21) (150 mg, 0.155 mmol) and 4-ethynyl benzoic acid (28.2 mg, 0.193 mmol). Complex 1b was obtained as a yellow solid. Yield: 62.1 mg, 0.0577 mmol; 37.2 %. ¹H NMR (400 MHz, [D6]-DMSO, 348 K, relative to SiMe4, δ /ppm): δ 0.80-0.85 (m, 6H, -CH3), 1.15-1.24 (m, 24H, -CH2-), 1.37-1.38 (m, 4H, -CH2-), 1.81-1.88 (m, 4H, -CH2-), 4.68-4.75 (m, 4H, -N-CH2-), 7.54-7.58 (m, 6H, phenyl and benzimidazolyl), 7.83-7.85 (m, 2H, phenyl), 8.01-8.06 (m, 2H, benzimidazolyl), 8.32-8.37 (m, 2H, benzimidazolyl), 8.41 (d, *J* = 8.0 Hz, 2H, benzimidazolyl), 8.49 (t, *J* = 8.0 Hz, 1H, pyridine). HRMS (Positive ESI): calcd for C₄₈H₅₈N₅O₂Pt, *m*/*z* 931.4212; found: 931.4212 [M-PF6]⁺. Elemental analysis calcd (%) for C₄₈H₅₈F₆N₅O₂PPt•2CHCl₃: C, 45.64; H, 4.60; N, 5.32; found: C, 45.71; H, 4.81; N, 5.13.

[Pt{bzimpy(C₁₀H₂₁)₂}{C=C-C₆H₄-(COOCH₂-C₆H₄-NO₂-2)-2}]PF₆ (2a). This was synthesized from [Pt(R₂-Bzimpy)Cl]PF₆ (R = C₁₀H₂₁) (150 mg, 0.155 mmol) and 2-nitrobenzyl 2-ethynylbenzoate (63.2 mg, 0.225 mmol). Complex **2a** was obtained as a yellow solid. Yield: 83.1 mg, 0.0686 mmol; 44.3 %. ¹H NMR (400 MHz, [D₆]-DMSO, 298 K, relative to SiMe₄, δ /ppm): δ 0.83 (t, *J* = 6.5 Hz, 6H, -CH₃), 1.20–1.28 (m, 24H, -CH₂-), 1.38–1.43 (m, 4H, -CH₂-), 1.86–1.90 (m, 4H, -CH₂-), 4.78 (t, *J* = 6.5 Hz, 4H, -N-CH₂-), 5.57 (s, 2H, -OCH₂-), 7.31 (t, *J* = 7.4 Hz, 1H, phenyl), 7.43–7.49 (m, 3H, phenyl and benzimidazolyl), 7.51–7.57 (m, 3H, phenyl and benzimidazolyl), 7.64 (d, *J* = 7.4 Hz, 1H, phenyl), 7.71 (d, *J* = 7.4 Hz, 1H, phenyl), 7.86–7.90 (m, 4H, benzimidazolyl), 7.96 (d, *J* = 7.4 Hz, 1H, phenyl), 8.41–8.44 (m, 2H, phenyl),

8.47–8.56 (m, 3H, pyridine). HRMS (Positive ESI): calcd for C₅₅H₆₃N₆O₄Pt, *m/z* 1066.4557; found: 1066.4554 [M–PF₆]⁺. Elemental analysis calcd (%) for C₅₅H₆₃F₆N₆O₄PPt•0.5CHCl₃: C, 52.41; H, 5.03; N, 6.61; found: C, 52.58; H, 5.05; N, 6.49.

[Pt{bzimpy(C₁₀H₂₁)₂}{C=C-C₆H₄-(COOH)-2}]PF₆ (2b). This was synthesized from [Pt(R₂-Bzimpy)Cl]PF₆ (R = C₁₀H₂₁) (150 mg, 0.155 mmol) and 2-ethynyl benzoic acid (28.2 mg, 0.193 mmol). Complex 2b was obtained as a yellow solid. Yield: 59.2 mg, 0.0550 mmol; 35.5 %. ¹H NMR (400 MHz, [D₆]-DMSO, 298 K, relative to SiMe₄, δ /ppm): δ 0.76-0.85 (m, 6H, -CH₃), 1.15-1.25 (m, 24H, -CH₂-), 1.41-1.49 (m, 4H, -CH₂-), 1.91-1.99 (m, 4H, -CH₂-), 4.82-4.93 (m, 4H, -N-CH₂-), 7.03-7.05 (m, 2H, phenyl), 7.36-7.42 (m, 2H, benzimidazolyl), 7.55-7.60 (m, 4H, benzimidazolyl), 7.95-7.99 (m, 1H, phenyl), 8.07-8.09 (m, 2H, benzimidazolyl), 8.21 (d, *J* = 7.4 Hz, 1H, phenyl), 8.57-8.63 (m, 3H, pyridine). HRMS (Positive ESI): calcd for C₄₈H₅₈N₅O₂Pt, *m/z* 931.4237; found: 931.4200 [M-PF₆]⁺. Elemental analysis calcd (%) for C₄₈H₅₈F₆N₅O₂PPt•2CHCl₃: C, 45.64; H, 4.60; N, 5.32; found: C, 45.86; H, 4.77; N, 5.13.

8

Complex	Absorption
	λ _{max} / nm
	$(\varepsilon_{\rm max} / {\rm dm}^3 {\rm mol}^{-1} {\rm cm}^{-1})$
$[Pt{bzimpy(C_{10}H_{21})_2}{C=C-C_6H_4-}$	310 (51650), 350 (36670), 375sh (29200),
$(COOCH_2 - C_6H_4 - NO_2 - 2) - 4\}]PF_6 (1a)$	434 (6900)
$[Pt{bzimpy(C_{10}H_{21})_2}{C=C-C_6H_4-(COOH)-4}]PF_6 (1b)$	305 (37570), 353 (30650), 436 (4900)
$[Pt{bzimpy(C_{10}H_{21})_2}{C=C-C_6H_4-(COOCH_2-C_6H_4-NO_2-2)-2}]PF_6 (2a)$	325 (49400), 353 (45940), 373sh (37950),
	438 (5900)
$[Pt{bzimpy(C_{10}H_{21})_2}{C=C-C_6H_4-(COOH)-2}]PF_6 (2b)$	300 (37120), 354 (27560), 440 (2000)

Table S1Electronic absorption data of complexes 1a-2b in DMSO at 298 K

Table S2	Dynamic light scattering (DLS) data of 1a and 2a in 50 % DMSO-water

mixtures at 298 K

Complex	Hydrodynamic
	diameter / nm
$Pt{bzimpy(C_{10}H_{21})_2}{C=C-C_6H_4-(COOCH_2-C_6H_4+C_6H_4-C_6H_4+C_6H_6+C_6C_6H_6+C_6H_6+C_6H_6-C_6H_4-C_6H_6+C_6H_6$	136±42
$NO_{2}-2)-4$]PF ₆ (1a)	
$[Pt\{bzimpy(C_{10}H_{21})_2\}\{C{\equiv}C{-}C_6H_4{-}(COOCH_2{-}C_6H_4{-}$	146±28
$NO_{2}-2)-2$]PF ₆ (2a)	



Figure S1 Electronic absorption spectra of 1a–2b in DMSO at 298 K.



Figure S2 UV-Vis absorption traces of **2a** in DMSO at 298 K upon increasing the water content from 0 to 90 %.



Figure S3 Normalized emission spectral traces of 1a in DMSO at 298 K upon increasing the water content from 50 to 90 %.



Figure S4 Emission spectral traces of **2a** in DMSO at 298 K upon increasing the water content from 0 to 90 %.



Figure S5 Normalized emission spectral traces of 2a in DMSO at 298 K upon increasing the water content from 50 to 90 %.



Figure S6 Emission spectral changes of **1a** in DMSO–water mixtures (20:80, v/v) upon increasing temperature from 298 to 348 K.



Figure S7 Normalized emission spectra of 1a in DMSO–water mixtures (20:80, v/v) upon increasing temperature from 298 to 348 K.



Figure S8 UV-Vis absorption spectral traces of **2a** in DMSO at 298 K upon prolonged UV irradiation at 290 nm. The direction of arrows indicates the direction of spectral changes upon UV irradiation.



Figure S9 ¹H NMR spectral traces of **1b** in [D₆]-DMSO at different temperatures showing the aryl region.



Figure S10 Temperature-dependent UV-vis absorption spectral changes of 1b in DMSO upon cooling from 348 to 298 K. The direction of arrows indicates the direction of spectral changes upon cooling.



Figure S11 TEM image of 1b prepared from a DMSO solution. Inset: the corresponding SAED pattern.



Figure S12Powder X-ray diffraction pattern of a solid sample of 1b. Numerical
values indicate the *d*-spacings (Å).



Figure S13 (a) High-resolution positive-ion ESI mass spectrum of 1a after UV irradiation at 310 nm. (b) Expanded ion cluster of 1a corresponding to [M–PF₆]⁺ and (c) its simulated isotopic pattern. (d) Expanded ion cluster of 1a corresponding to [M–CH₂–C₆H₄–NO₂–PF₆]⁺ and (e) its simulated isotopic pattern.



Figure S14 (a) High-resolution positive-ion ESI mass spectrum of 2a after UV irradiation at 310 nm. (b) Expanded ion cluster of 2a corresponding to [M–PF₆]⁺ and (c) its simulated isotopic pattern. (d) Expanded ion cluster of 2a corresponding to [M–CH₂–C₆H₄–NO₂–PF₆]⁺ and (e) its simulated isotopic pattern.



Figure S15 TEM images of 2a prepared from a DMSO solution (a) before and (b) after UV irradiation.



Figure S16 TEM image of 2b prepared from a DMSO solution.



Figure S17 ¹H NMR spectra of **1a** in [D₆]-DMSO at 298 K (a) before and (b) after UV irradiation. The integral of the $-CH_2-C_6H_4-NO_2$ has been labelled and calibrated by the terminal methyl group on the bzimpy ligand.



Figure S18Partial ¹H NMR spectra of 1a in $[D_6]$ -DMSO at 298 K (a) before and (b)after UV irradiation. The integral of the $-CH_2-C_6H_4-NO_2$ has beenlabelled and calibrated by the pyridine group on the bzimpy ligand.



Figure S19 Partial ¹H NMR spectra of 1a in [D₆]-DMSO showing the aryl region at 298 K (a) before and (b) after UV irradiation.



Figure S20 Partial ¹H NMR spectra of **1a** in [D₆]-DMSO showing the aryl region after UV irradiation at (a) 298 K and (b) 348 K.

References

- 1. R. H. Pawle, V. Eastman, and S. W Thomas, J. Mater. Chem. 2011, 21(36), 14041.
- F. A. Mandl, V. C. Kirsch, I. Ugur, E. Kunold, J. Vomacka, C. Fetzer, S. Schneider, K. Richter, T. M. Fuchs, I. Antes, and S. A. Sieber, *Angew. Chem. Int. Ed. 2016*, 55(47), 14852.
- A. Y. Y. Tam, W. H Lam, K. M. C. Wong, N. Zhu, and V. W. W. Yam, *Chem. –Eur. J. 2008*, 14(15), 4562.
- A. F. F. Cheung, E. Y. H. Hong, and V. W. W. Yam, *Chem. –Eur. J. 2018*, 24(6), 1383.