Electronic Supplementary Information for

Interrogating the Photogenerated Ir(IV) State of a Water Oxidation Catalyst using Ultrafast Optical and X-ray Absorption Spectroscopy

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I. Experimental details

A. General

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Solvents for synthesis were ACS reagent grade, unless otherwise specified. Column chromatography was performed with standard grade silica gel (Sorbent Technologies, 60 Å, 32-63 μm) and alumina deactivated to Activity III (Sigma-Aldrich, activated, neutral, Brockmann I). CH₂Cl₂ used in spectroscopy was dried using a GlassContour solvent system, and benzonitrile was distilled and further dried using activated alumina. ¹H and ¹³C nuclear magnetic resonance spectra were recorded on a Bruker Avance III 500 MHz (with chemical shifts in ppm referenced to the solvent), and high resolution electrospray ionization (HR-ESI) mass spectra were recorded on an Agilent 6210 LC-TOF. Characterization studies were performed at the Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern University.

B. Synthesis

Reagents 2-phenylpyridin-4-ylamine (NH₂-ppy)¹, [Cp*IrCl₂]₂, N-(2,5-di-tert-butyphenyl)naphthalene-1,8-dicarboxyanhydride-4,5-dicarboximide (NIA)³, and 3,5-di-tert-butylphenylboronic acid⁴ were synthesized according to reported methods.

PMI–C₅ (1)

PMI–C₅ (1). Perylene-3,4:9,10-bis(dicarboxylic anhydride) (31.5 g, 80.3 mmol), 3-aminopentane (3.68 g, 4.92 mL, 42.3 mmol), zinc (II) acetate dihydrate (11.9 g, 54.1 mmol), imidazole (161 g, 2.37 mol), and water (80 mL) were combined in a teflon sleeve and placed in a
high pressure autoclave. The vessel was sealed, and the temperature was gradually increased to 190 °C. After 24 h the heat was turned off and the reaction cooled to room temperature. The dark red-brown crude product was removed from the sleeve with 2 M HCl and vacuum filtered, and the product was extracted from the filter cakes by stirring the solid repeatedly in CHCl₃. Column chromatography on silica was performed with CHCl₃ as the eluent, and first red band afforded the target product. Yield: 8.54 g (21.8 mmol, 27%). ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, J = 7.9 Hz, 2H), 8.29 (d, J = 7.6 Hz, 2H), 8.25 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 5.08 (tt, J = 9.5, 5.9 Hz, 1H), 2.28 (m, 2H), 1.96 (m, 2H), 0.94 (t, J = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 136.71, 134.17, 130.74, 129.80, 129.06, 127.77, 126.90, 126.46, 123.46, 120.00, 77.41, 77.36, 77.16, 76.91, 57.40, 25.17, 11.60. MS (ESI): m/z 392.163 [M+H]⁺ (calculated 392.165).

Br–PMI–C₅ (2). PMI–C₅ (1) (2.00 g, 5.11 mmol) was dissolved in 400 mL CH₂Cl₂ and heated to 40 °C under N₂. Br₂ (0.26 mL, 5.1 mmol) was syringed in dropwise through the top of the condenser, and the solution was heated to reflux (50 °C) for 2 h. The solvent and bromine were evaporated off overnight, and the crude product was purified on a silica column with CHCl₃ as the eluent. Yield: 2.35 g (5.01 mmol, 98%). ¹H NMR (500 MHz, CDCl₃) δ 8.56 (t, J = 7.8 Hz, 2H), 8.44 (d, J = 7.5 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 5.08 (tt, J = 9.5, 5.9 Hz, 1H), 2.27 (m, 2H), 1.94 (m, 2H), 0.93 (t, J = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 136.34, 136.20, 133.00, 131.28, 130.91, 129.98, 129.93, 129.70, 129.35, 129.22,
129.16, 128.20, 127.13, 126.35, 126.10, 124.32, 123.73, 123.67, 120.77, 120.50, 120.29, 57.51, 25.17, 11.54. MS (ESI): m/z 470.073 [M+H]^+ (calculated 470.076).

H$_2$N–PMI–C$_5$ (3). Br–PMI–C$_5$ (2) (400 mg, 0.851 mmol) was combined with sodium azide (1.66 g, 25.5 mmol) in 10 mL N,N-dimethylacetamide (DMA) that had been dried with activated alumina. The solution was heated at 105 °C under N$_2$ for 5 h, and the cooled product was extracted into CH$_2$Cl$_2$ and washed with water (3 x 20 mL) to remove most of the DMA. The solvent was removed under vacuum and the crude product was purified on a silica column with 50:1 CH$_2$Cl$_2$/acetone as the eluent, affording a deep purple solid. Yield: 199 mg (0.490 mmol, 57%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.48 (m, 2H), 8.41 (d, $J = 7.4$ Hz, 1H), 8.29 (d, $J = 7.9$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 8.12 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 1H), 5.10 (m, 1H), 4.62 (s, 2H), 2.28 (m, 2H), 1.94 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.85, 145.76, 138.33, 137.43, 130.44, 129.88, 128.91, 126.32, 126.12, 125.83, 124.42, 123.50, 123.21, 120.04, 119.55, 117.89, 111.08, 57.25, 25.20, 11.56. MS (ESI): m/z 407.174 [M+H]$^+$ (calculated 407.176).

trityl–NH–PMI–C$_5$ (4). H$_2$N–PMI–C$_5$ (3) (460 mg, 1.31 mmol) was combined with trityl chloride (694 mg, 2.49 mmol), and 4-(dimethylamino)pyridine (14 mg, 0.11 mmol) in 30 mL
CH$_2$Cl$_2$ and stirred in an ice bath. Triethylamine (TEA) (0.31 mL, 2.2 mmol) was added dropwise, and the mixture was stirred at 0 °C for 1.5 h. The solvent was removed under vacuum, and the crude product was purified on a silica column deactivated with 2% TEA with CH$_2$Cl$_2$ as the eluent, yielding a deep blue solid. Yield: 648 mg (1.00 mmol, 88%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.43 (d, $J = 7.8$ Hz, 1H), 8.35 (d, $J = 7.6$ Hz, 1H), 8.20 (d, $J = 8.2$ Hz, 1H), 8.17 (d, $J = 8.1$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.45 (m, 6H), 7.34 (m, 6H), 7.30 (m, 3H), 6.35 (s, 1H), 6.21 (d, $J = 8.6$ Hz, 1H), 5.07 (tt, $J = 9.5$, 5.9 Hz, 1H), 2.27 (m, 2H), 1.92 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.96, 144.62, 144.09, 138.19, 137.26, 130.22, 129.98, 129.14, 128.69, 128.50, 128.06, 128.04, 127.55, 127.39, 126.00, 125.80, 125.51, 123.96, 123.70, 122.31, 119.25, 118.33, 117.46, 111.89, 72.05, 57.15, 25.17, 11.58. MS (ESI): $m/z$ 648.277 M$^+$ (calculated 648.278).

trityl–NH–PMA (5). trityl–NH–PMI–C$_5$ (4) (310 mg, 0.478 mmol) was combined with 2.21 g 85% KOH (33.4 mmol) in 15 mL t-BuOH and heated to reflux (105 °C) under N$_2$ for 41 h. The orange-brown solution was cooled slightly and 5 mL acetic acid was added, which accomplished the ring-closing to the anhydride and resulted in a thick blue-purple suspension. The product was extracted into CH$_2$Cl$_2$ and washed with water (3 x 25 mL), followed by column chromatography on silica deactivated with 1% TEA (eluent gradient: CH$_2$Cl$_2$ to 99:1 CH$_2$Cl$_2$/acetone), affording a blue solid. Yield: 128 mg (0.221 mmol, 46%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.46 (d, $J = 7.5$ Hz, 1H), 8.43 (d, $J = 8.2$ Hz, 1H), 8.25 (d, $J = 2.4$ Hz, 1H), 8.23
(d, J = 2.5 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 2.8 Hz, 1H), 7.79 (d, J = 3.3 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.42 (m, 6H), 7.36 (m, 6H), 7.31 (m, 3H), 6.49 (s, 1H), 6.27 (d, J = 8.7 Hz, 1H).  

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.49, 161.28, 145.29, 144.38, 140.31, 139.29, 133.78, 133.29, 129.50, 129.10, 128.86, 128.59, 128.08, 128.05, 127.68, 126.76, 126.48, 126.07, 125.12, 123.61, 123.38, 119.56, 117.73, 116.13, 113.21, 112.09, 72.23.  

MS (ESI): m/z 580.188 [M+H]$^+$ (calculated 580.191).


trityl–NH–PMI–ppy (6). trityl–NH–PMA (5) (200 mg, 0.345 mmol) was combined with NH$_2$–ppy (835 mg, 4.91 mmol) in 10 mL dry pyridine, to which 5 mg Zn(OAc)$_2$ (0.03 mmol) was added, and the solution was heated at 135 °C for 42 hours. The solvent was removed under vacuum, and the crude product was purified on an alumina column with 9:1 CH$_2$Cl$_2$/acetone as the eluent to yield a blue solid. Yield: 197 mg (0.269 mmol, 78%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 8.85 (d, J = 5.1 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 8.14 (dd, J = 11.3, 8.1 Hz, 2H), 8.06 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 1.7 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.48 (m, 6H), 7.43 (m, 2H), 7.35 (m, 6H), 7.32 (m, 3H), 7.29 (m, 2H), 6.48 (s, 1H), 6.25 (d, J = 8.6 Hz, 1H).  

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) $\delta$ 163.85, 163.72, 159.19, 151.17, 145.52, 145.09, 145.00, 139.40, 139.31, 138.55, 132.11, 131.67, 130.85, 129.90, 129.69, 129.52, 129.21, 128.87, 127.96, 127.48, 126.52, 126.40, 126.24, 125.00, 124.03, 123.40, 123.15, 121.53, 120.32, 119.76, 118.38, 117.86, 117.76, 112.43, 72.54. MS (ESI): m/z 732.265 [M+H]$^+$ (calculated 732.265).
NDI–PMI–ppy (8). trityl–NH–PMA (5) (100 mg, 0.137 mmol) was dissolved in 10 mL CH₂Cl₂, and a solution of trifluoroacetic acid (0.31 mL, 4.0 mmol) in 10 mL CH₂Cl₂ was added slowly while stirring at room temperature. After 20 min, the solvent was blown off with N₂ to yield the trityl-deprotected compound. To the same flask were added 1.56 g NIA (3.42 mmol), 10 mL dry pyridine, and 5 mg Zn(OAc)₂ (0.03 mmol), and the mixture was stirred under N₂ at 135 °C for 24 h. The solvent was removed under vacuum, and the crude product was dissolved in CH₂Cl₂ and washed with 1M HCl (3 x 20 mL). The compound was purified on an alumina column with 24:1 CHCl₃/acetone, followed by a silica column with 47:3 CH₂Cl₂/acetone as the eluent, yielding a deep red solid. Yield: 113 mg (0.122 mmol, 89%). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.91 (d, J = 5.0 Hz, 1H), 8.86 (d, J = 5.4 Hz, 4H), 8.33 (dd, J = 16.6, 7.8 Hz, 1H), 8.29 (dd, J = 7.9, 3.4 Hz, 1H), 8.24 (dd, J = 8.2, 4.4 Hz, 1H), 8.11 (dd, J = 15.7, 7.3 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.99 (dd, J = 24.0, 8.0 Hz, 1H), 7.94 (t, J = 3.7 Hz, 2H), 7.64 (m, 3H), 7.55 (dd, J = 8.5, 2.2 Hz, 1H), 7.49 (t, J = 7.5, 1H), 7.42 (m, 3H), 7.35 (m, 1H), 7.08 (d, J = 2.1 Hz, 1H), 1.36 (s, 9H), 1.30 (d, J = 3.8 Hz, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 163.81, 163.80, 163.19, 159.33, 151.06, 150.63, 144.22, 143.77, 138.93, 137.00, 136.97, 136.56, 136.54, 134.11, 134.07, 132.00, 131.87, 131.73, 130.98, 130.93, 130.50, 129.78, 129.75, 129.58, 129.56, 129.34, 129.27, 129.24, 128.83, 128.59, 128.52, 128.34, 128.24, 127.71, 127.59, 127.54, 127.24, 126.99,
NDI–PMI–Ir catalyst (9). NDI–PMI–ppy ligand (8) (75 mg, 0.081 mmol) was dissolved in 12 mL N2-sparged CH2Cl2, to which [Cp*IrCl2]2 (32 mg, 0.40 mmol) and NaOAc·3H2O (22 mg, 0.16 mmol) were added. The mixture was stirred at 35 °C under N2 for 9 h, and the product was filtered twice through celite with CH2Cl2 and the solvent removed under vacuum to afford a deep red solid. Yield: 106 mg (0.082 mmol, quantitative). 1H NMR (500 MHz, CD2Cl2) δ 8.90 (d, J = 1.1 Hz, 4H), 8.87 (d, J = 6.0 Hz, 1H), 8.65 (m, 2H), 8.62 (d, J = 8.5 Hz, 1H), 8.52 (d, J = 7.3 Hz, 1H), 8.48 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 7.7, 1.2 Hz, 1H), 7.74 (m, 3H), 7.66 (m, 2H), 7.55 (dd, J = 8.6, 2.2 Hz, 1H), 7.25 (dd, J = 6.1, 2.2 Hz, 1H), 7.22 (t, J = 7.3, 1H), 7.08 (dd, J = 2.2, 1.4 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 1.73 (s, 15H), 1.35 (d, J = 1.6 Hz, 9H), 1.29 (d, J = 4.0 Hz, 9H). 13C NMR (125 MHz, CD2Cl2) δ 169.08, 164.42, 164.38, 163.64, 163.45, 152.52, 151.16, 145.10, 144.84, 144.67, 144.64, 137.50, 137.07, 137.04, 136.38, 134.87, 133.06, 132.25, 132.15, 132.10, 132.03, 131.38, 131.35, 131.27, 130.70, 130.09, 129.88, 129.64, 129.05, 129.03, 128.99, 128.88, 128.85, 128.16, 127.99, 127.96, 127.93, 127.28, 127.08, 126.78, 125.28, 125.21, 125.13, 125.08, 124.83, 124.45, 123.65, 122.53, 121.62, 121.56, 121.24, 121.08, 120.28, 89.40, 36.04, 34.77, 32.02, 31.48, 9.31. MS (ESI): m/z 1253.384 [M–Cl] + (calculated 1253.383).
4-bromo-1,8-naphthalic anhydride (2.00 g, 7.22 mmol) and octylamine (7.1 mL, 43 mmol) were combined in 70 mL glacial acetic acid and stirred at 125 °C for 26 h. 70 mL water was added to precipitate the product, which was vacuum filtered and purified on a silica column with 4:1 CH₂Cl₂/hexanes as the eluent, yielding a white solid. Yield: 375 mg (5.70 mmol, 79%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.64 (d, \(J = 7.2\) Hz, 1H), 8.54 (d, \(J = 8.4\) Hz, 1H), 8.39 (dd, \(J = 8.0\), 1H), 8.02 (d, \(J = 7.8\) Hz, 1H), 7.83 (t, \(J = 7.9\) Hz, 1H), 4.15 (t, \(J = 7.5\) Hz, 2H), 1.71 (p, \(J = 7.5\) Hz, 2H), 1.40 (m, 2H), 1.34 (m, 2H), 1.26 (m, 6H), 0.86 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 163.72, 163.69, 133.31, 132.12, 131.31, 131.19, 130.70, 130.30, 129.08, 128.18, 123.25, 122.39, 40.77, 31.95, 29.47, 29.36, 28.22, 27.27, 22.78, 14.25. MS (ESI): \(m/z\) 388.090 [M+H] \(^+\) (calculated 388.091).

To 120 mL N₂-purged tetrahydrofuran were added Br–NMI–C₈ (1.25 g, 3.22 mmol) and 3,5-di-tert-butylphenylboronic acid (2.72 g, 11.6 mmol), and the mixture was heated to 50 °C. 370 mg Pd(PPh₃)₄ (0.320 mmol, 10 mol %) was added under N₂ along with 40 mL
deoxygenated Na$_2$CO$_3$ (1.6 M), and the mixture was stirred at 70 °C for 14 h. The crude product was extracted into CH$_2$Cl$_2$, and the solvent was removed under vacuum and the product purified on a silica column with 7:3 CH$_2$Cl$_2$/hexanes as the eluent, affording an off-white solid. Yield: 1.18 g (2.37 mmol, 74%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.65 (d, $J$ = 7.7 Hz, 1H), 8.63 (dd, $J$ = 7.5, 1.0 Hz, 1H), 8.30 (dd, $J$ = 8.5, 1.0 Hz, 1H), 7.73 (d, $J$ = 7.5 Hz, 1H), 7.71 (dd, $J$ = 7.5 Hz, 8.5 Hz, 1H), 7.57 (t, $J$ = 1.8 Hz, 1H), 7.33 (d, $J$ = 1.8 Hz, 2H), 4.21 (t, $J$ = 8.0 Hz, 2H), 1.75 (p, $J$ = 7.5 Hz, 2H), 1.44 (m, 2H), 1.40 (s, 18H), 1.28 (m, 8H), 0.87 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.56, 164.36, 151.27, 148.24, 138.15, 133.02, 131.23, 130.99, 130.38, 128.87, 127.99, 126.81, 124.42, 123.01, 122.52, 121.58, 40.66, 35.17, 31.98, 31.65, 29.53, 29.40, 28.30, 27.32, 22.80, 14.27. MS (ESI): $m/z$ 498.336 [M+H]$^+$ (calculated 498.337).

4-[3,5-di-tert-butylphenyl]-1,8-naphthalic anhydride [(di-tert-butyl)ph–NMA]. (di-tert-butyl)ph–NMI–C$_8$ (925 mg, 1.86 mmol) and 2.45 g 85% KOH (37.1 mmol) were combined in 23 mL t-BuOH, and the mixture was heated at 100 °C for 1 h. The mixture was acidified with 12 mL glacial acetic acid, and the product was extracted into CH$_2$Cl$_2$ and washed with water (3 x 25 mL). Solvent was evaporated under vacuum and the crude product was purified on a silica column with CH$_2$Cl$_2$ as the eluent, giving a white solid. Yield: 716 mg (1.85 mmol, 99%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 (dd, $J$ = 8.5, 7.3 Hz, 2H), 8.41 (d, $J$ = 8.6 Hz, 1H), 7.78 (m, 2H), 7.59 (d, $J$ = 1.9 Hz, 1H), 7.32 (d, $J$ = 1.7 Hz, 2H), 1.40 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.09, 160.85, 151.55, 150.03, 137.46, 134.64, 133.49, 133.25, 131.12, 130.68,
128.50, 127.31, 124.27, 123.02, 119.05, 117.42, 35.20, 31.63. MS (ESI): m/z 387.194 [M+H]^+ (calculated 387.196).

**NMI–PMI–ppy (10)**

**NMI–PMI–ppy (10).** trityl–NH–PMA (5) (30 mg, 0.041 mmol) was dissolved in 5 mL CH$_2$Cl$_2$, and a solution of trifluoroacetic acid (0.047 mL, 0.61 mmol) in 5 mL CH$_2$Cl$_2$ was added slowly while stirring at room temperature. After 1 h, the solvent was blown off with N$_2$ to yield the trityl-deprotected compound. To the same flask were added 79 mg (di-$t$-butyl)ph–NMA (0.20 mmol), 4 g imidazole, and 5 mg Zn(OAc)$_2$ (0.03 mmol), and the mixture was stirred under N$_2$ at 155 °C for 17 h. The product was extracted into CH$_2$Cl$_2$ and washed with 1 M HCl (3 x 25 mL) to remove the imidazole. The compound was first purified on silica column with 19:1 CH$_2$Cl$_2$ acetone as the eluent, followed by an alumina column with 97:3 CHCl$_3$/acetone as the eluent, yielding a deep red solid. Yield: 34 mg (0.040 mmol, 98%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.94 (d, $J = 5.1$ Hz, 1H), 8.76 (d, $J = 7.5$ Hz, 1H), 8.74 (dd, $J = 7.1$, 1.2 Hz, 1H), 8.49 (d, $J = 7.9$ Hz, 1H), 8.44 (m, 2H), 8.38 (d, $J = 8.1$ Hz, 1H), 8.26 (d, $J = 7.4$ Hz, 1H), 8.19 (d, $J = 8.2$ Hz, 1H), 8.14 (d, $J = 8.1$ Hz, 1H), 8.06 (m, 2H), 7.87 (d, $J = 1.8$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.79 (dd, $J = 8.7$, 7.1 Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.61 (t, $J = 1.8$ Hz, 1H), 7.52 (m, 1H), 7.45 (m, 2H), 7.40 (m, 4H), 1.42 (s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.74, 164.52, 163.36, 163.32, 159.38, 151.47, 151.04, 149.35, 144.35, 139.01, 137.94, 137.41, 137.05, 135.35, 134.06, 132.11, 131.96, 131.93, 131.85, 131.25, 130.77, 130.04, 129.74, 129.62, 129.59, 129.29, 128.87, 128.84, 128.47, 128.38, 128.29, 127.29, 127.10, 126.44,
NMI–PMI–Ir catalyst (11). NMI–PMI–ppy ligand (10) (25 mg, 0.029 mmol) was dissolved in 7 mL N₂-sparged CH₂Cl₂, to which [Cp*IrCl₂]₂ (12 mg, 0.015 mmol) and NaOAc·3H₂O (7.9 mg, 0.058 mmol) were added. The mixture was stirred at 35 °C under N₂ for 23 h, and the product was filtered twice through celite with CH₂Cl₂ and the solvent removed under vacuum to afford a deep red solid. Yield: 36 mg (0.030 mmol, quantitative). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.89 (d, J = 6.1 Hz, 1H), 8.73 (m, 2H), 8.48 (d, J = 7.9 Hz, 1H), 8.44 (m, 2H), 8.38 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 2.2 Hz, 1H), 7.83 (m, 3H), 7.78 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.63 (t, J = 1.8 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 7.42 (d, J = 1.9 Hz, 2H), 7.35 (dd, J = 6.0, 2.0 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 1.73 (s, 15H), 1.42 (s, 18H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 169.05, 165.05, 164.84, 164.39, 163.52, 153.82, 152.52, 151.87, 149.58, 145.20, 144.83, 138.43, 137.82, 137.43, 136.33, 136.08, 134.27, 132.18, 132.14, 131.89, 131.63, 131.30, 131.13, 130.24, 129.97, 129.95, 129.03, 128.98, 128.79, 128.67, 127.52, 126.83, 125.98, 125.76, 125.15, 124.86, 124.82, 124.71, 123.70, 123.32, 123.22, 122.57, 121.84, 121.49, 121.44, 121.02, 120.93, 120.31, 89.36, 35.49, 31.76, 9.30. MS (ESI): m/z 1184.399 [M–Cl]⁺ (calculated 1184.398).
II. Figures

A. Steady-state spectroscopy

Figure S1. Steady-state absorption (blue) and emission (red) spectra of PMI–C₅ (1) in CH₂Cl₂.

B. Spectroelectrochemistry

Figure S2. (A) Spectroelectrochemical difference spectrum of radical anion of PMI–C₅ (1) (potential of −1.6 V applied, initial ground state absorption spectrum subtracted). (B) Spectroelectrochemical difference spectrum of radical cation of PMI–C₅ (1) (potential of +1.3 V applied, initial ground state absorption spectrum subtracted). Both spectra acquired in benzonitrile (0.1 M TBAPF₆).
C. Transient absorption spectroscopy

Figure S3. (A) Femtosecond transient absorption spectra of NMI–PMI–Ir catalyst (11) in PhCN following 150 fs, 500 nm laser pulse excitation. (B) Spectra associated with the kinetic components obtained by global analysis of the transient absorption spectra of 11 in PhCN.

Figure S4. (A) Femtosecond transient absorption spectra of NDI–PMI–ppy ligand (8) in PhCN following 150 fs, 500 nm laser pulse excitation. (B) Spectra associated with the kinetic components obtained by global analysis of the transient absorption spectra of 8 in PhCN.
Figure S5. (A) Femtosecond transient absorption spectra of NDI–PMI–Ir catalyst triad (9) in PhCN following 150 fs, 500 nm laser pulse excitation. (B) Spectra associated with the kinetic components obtained by global analysis of the transient absorption spectra of 9 in PhCN.

Figure S6. Nanosecond transient absorption spectra of NDI–PMI–Ir(III) catalyst (9) in PhCN following 150 fs, 500 nm laser pulse excitation. (Inset: transient absorption kinetic trace at 540 nm with least squares fit to the data shown.)
D. Energy level diagram

![Energy level diagram](image)

**Figure S7.** Energy level diagram for the NDI–PMI–Ir catalyst triad in PhCN, showing the photophysical pathways accessible from the PMI excited state.

E. Time-resolved X-ray absorption

![Time-resolved X-ray absorption](image)

**Figure S8.** Difference spectra between ground state and photoexcited state at 100 ps (black), 153.6 ns (red), and 307.1 ns (green). Since NDI$^{\text{−}}$–PMI–Ir(IV) recombines to the Ir(III) state in ~20 ns, there are no transient changes in later X-ray bunches, further confirming that changes seen in the 100 ps spectrum are real and are separate from the noise of the experiment.
III. Supporting tables

**Table S1.** Ion-pair Distances and Energies for Electron Transfer Products in Triad 9 in PhCN

<table>
<thead>
<tr>
<th>Ion Pair</th>
<th>$r_{DA}$ (Å)</th>
<th>$\Delta G_{IP}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI$^{-}$--PMI$^{++}$--Ir(III)</td>
<td>8.7</td>
<td>1.93</td>
</tr>
<tr>
<td>NDI--PMI$^{+}$--Ir(IV)</td>
<td>12.0</td>
<td>1.67</td>
</tr>
<tr>
<td>NDI$^{-}$--PMI--Ir(IV)</td>
<td>20.6</td>
<td>1.31</td>
</tr>
</tbody>
</table>

**Table S2.** Timescales for Charge Separation ($\tau_{CS}$), Charge Recombination ($\tau_{CR}$), and Charge Shift ($\tau_{CSH}$) in Compounds 8, 9, and 11 in PhCN, with Corresponding Timescales in Figure S7

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_{CS}$ (ps)</th>
<th>$\tau_{CSH}$ (ps)</th>
<th>$\tau_{CR}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI–PMI–ppy (8)</td>
<td>2.9 ± 0.4 ($\tau_2$)</td>
<td>--</td>
<td>56 ± 5 ($\tau_6$)</td>
</tr>
<tr>
<td>NDI–PMI–Ir(III) (9)</td>
<td>1.5 ± 0.4 ($\tau_2$, $\tau_3$)</td>
<td>17 ± 2 ($\tau_4$, $\tau_5$)</td>
<td>20800 ± 100</td>
</tr>
<tr>
<td>NMI–PMI–Ir(III) (11)</td>
<td>3.4 ± 0.2 ($\tau_3$)</td>
<td>--</td>
<td>36 ± 2 ($\tau_7$)</td>
</tr>
</tbody>
</table>

IV. References