**Supporting information for:** 

## Excited-State Triplet Equilibria in a Series of Re(I)-Naphthalimide Bichromophores

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## 1. Synthetic Details and Structural Characterization

*Synthesis of 2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI). p*-Toluidine (10.16 mmol, 1.09 g), 1,8-naphthalic anhydride (9.24 mmol, 1.82 g), and 50 mL of glacial acetic acid were added to a 150 mL pressure vessel and heated to 140 °C for 6 hours. Once cool, 25 mL of distilled water was added to the solution and the white precipitate was filtered on a glass frit. The solid was washed with 200 mL of water and dried overnight under vacuum. The crude solid was filtered using the isolera automated flash column with a silica column and eluted with dichloromethane/hexanes in a 3:1 ratio. The solvent was removed and the white solid was obtained in 60% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  8.60 (dd, J = 7.2, 1.1 Hz, 2H), 8.31 (dd, J = 8.1, 1.2 Hz, 2H), 7.81 (dd, J = 8.3, 7.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 288.1027 [M+H]<sup>+</sup>, calcd (C<sub>19</sub>H<sub>14</sub>NO<sub>2</sub>) 288.1025. Anal. Calcd (found) for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>: C, 79.43 (79.14); H, 4.56 (4.81); N, 4.88 (4.87). ATR-FTIR: 490, 516, 538, 781, 812, 1185, 1234, 1352, 1373, 1514, 1587, 1656, 1673, 1699 cm<sup>-1</sup>.



Figure S1. <sup>1</sup>H NMR spectrum of NI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S2. <sup>1</sup>H NMR spectrum of NI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



Figure S3. HRMS of NI.

Synthesis of 2-(1,10-phenanthrolin-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI-phen). 5-Amino-1,10-phenanthroline (4.4 mmol, 859 mg), 1,8-naphthalic anhydride (4 mmol, 793 mg), and 20 mL of glacial acetic acid were added to a 75 mL pressure vessel and heated to 145 °C for 24 hours. Once cool, 15 mL of distilled water was added to the solution and the tan precipitate was filtered on a glass frit. The solid was washed with 250 mL of water and dried overnight under vacuum. The off-white solid was obtained in 52% yield (785 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ 9.31 – 9.22 (m, 2H), 8.71 (dd, J = 7.3, 1.1 Hz, 2H), 8.38 (dd, J = 8.4, 1.1 Hz, 2H), 8.31 (dd, J = 8.2, 1.8 Hz, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 1H), 7.91 – 7.84 (m, 3H), 7.71 (dd, J = 8.0, 4.4 Hz, 1H), 7.59 (dd, J = 8.3, 4.3 Hz, 1H).

Synthesis of  $Re(NI-phen)(CO)_3CI$ . Pentacarbonylchlororhenium(I) (1 mmol, 363 mg) was added to one equivalent of NI-phen (1 mmol, 374 mg) and 20 mL of toluene in a 50 mL round bottom flask. The solution was degassed, put under N<sub>2</sub>, and refluxed while mixing for 1 hour. After cooling, the yellow precipitate was filtered out on a glass frit and washed with 200 mL of toluene. The yellow solid was dried under vacuum overnight and was obtained in 98% yield (671 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.47 – 9.39 (m, 2H), 8.70 (ddd, J = 13.4, 7.3, 1.2 Hz, 2H), 8.65 (dd, J = 8.3, 1.4 Hz, 1H), 8.44 (dt, J = 8.3, 1.3 Hz, 2H), 8.37 (dd, J = 8.5, 1.4 Hz, 1H), 8.18 (s, 1H), 7.95 (dd, J = 8.2, 5.1 Hz, 1H), 7.90 (ddd, J = 8.5, 7.3, 1.6 Hz, 2H), 7.83 (dd, J = 8.5, 5.1 Hz, 1H).

*Synthesis of [Re(NI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re1).* Re(NI-phen)(CO)<sub>3</sub>Cl (0.25 mmol, 170 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from

solution. The yellow filtrate was added to an excess of dimethylaminopyridine (2.5 mmol, 305 mg) and the solution was then refluxed for an additional 3 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 200 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium hexafluorophosphate solution in water. The yellow solid was dried under vacuum overnight and was obtained in 99% yield (226 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.58 (ddd, J = 12.8, 5.2, 1.4 Hz, 2H), 8.82 (dd, J = 8.4, 1.4 Hz, 1H), 8.66 (ddd, J = 16.2, 7.3, 1.2 Hz, 2H), 8.51 (dd, J = 8.5, 1.4 Hz, 1H), 8.48 – 8.43 (m, 2H), 8.25 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.04 (dd, J = 8.5, 5.1 Hz, 1H), 7.90 (ddd, J = 8.3, 7.3, 4.6 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 6.27 (d, J = 7.4 Hz, 2H), 2.91 (s, 6H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 766.1224 [M–PF<sub>6</sub>]<sup>+</sup>, calcd (C<sub>34</sub>H<sub>23</sub>N<sub>5</sub>O<sub>5</sub><sup>185</sup>Re) 766.1229. Anal. Calcd (found) for C<sub>34</sub>H<sub>23</sub>F<sub>6</sub>N<sub>5</sub>O<sub>5</sub>PRe·0.5H<sub>2</sub>O: C, 44.30 (44.15); H, 2.62 (2.40); N, 7.60 (7.46). ATR-FTIR: 557, 730, 779, 838, 1234, 1350, 1587, 1626, 1673, 1709, 1903, 2058 cm<sup>-1</sup>.



Figure S4. <sup>1</sup>H NMR spectrum of [Re(NI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re1) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



**Figure S5**. <sup>1</sup>H NMR spectrum of [Re(NI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re1**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S6**. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of [Re(NI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re1**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S7. HRMS of [Re(NI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re1).

Synthesis of 6-bromo-2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**BrNI**). p-Toluidine (10.16 mmol, 1.09 g), 4-bromo-1,8-naphthalic anhydride (9.24 mmol, 2.56 g), and 50 mL of glacial acetic acid were added to a 150 mL pressure vessel and heated to 140 °C for 6 hours. Once cool, 25 mL of distilled water was added to the solution and the white precipitate was filtered on a glass frit. The solid was washed with 200 mL of water and dried overnight under vacuum. The crude solid was filtered using the isolera automated flash column with a silica column and eluted with dichloromethane/hexanes in a 3:1 ratio. The solvent was removed, and the off-white solid was obtained in 60% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  8.69 – 8.62 (m, 2H), 8.42 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 8.5, 7.3 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 366.0134 [M+H]<sup>+</sup>, calcd (C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub><sup>79</sup>Br)

366.0130. Anal. Calcd (found) for C<sub>19</sub>H<sub>12</sub>BrNO<sub>2</sub>: C, 62.32 (62.04); H, 3.30 (3.27); N, 3.82 (3.81). ATR-FTIR: 422, 500, 518, 730, 781, 814, 1193, 1238, 1344, 1365, 1589, 1656, 1707 cm<sup>-1</sup>.



Figure S8. <sup>1</sup>H NMR spectrum of BrNI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S9. <sup>1</sup>H NMR spectrum of BrNI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



Figure S10. HRMS spectrum of BrNI.

Synthesis of 6-bromo-2-(1,10-phenanthrolin-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (BrNI-phen). 5-Amino-1,10-phenanthroline (2.03 mmol, 396 mg), 4-bromo-1,8-naphthalic anhydride (1.85 mmol, 512 mg), and 10 mL of glacial acetic acid were added to a 75 mL pressure vessel and heated to 145 °C for 5 hours. Once cool, 5 mL of distilled water was added to the solution and the tan precipitate was filtered on a glass frit. The solid was washed with 250 mL of water and dried overnight under vacuum. The light brown solid was obtained in 59% yield (498 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  7.32 (dd, J = 17.8, 4.6 Hz, 2H), 6.81 (t, J = 7.6 Hz, 2H), 6.57 (d, J = 7.8 Hz, 1H), 6.35 (d, J = 8.1 Hz, 1H), 6.22 (d, J = 7.8 Hz, 1H), 6.08 (d, J = 8.3 Hz, 1H), 6.02 (t, J = 8.0 Hz, 1H), 5.95 (s, 1H), 5.80 – 5.59 (m, 2H).

Synthesis of  $Re(BrNI-phen)(CO)_3Cl$ . Pentacarbonylchlororhenium(I) (0.5 mmol, 181 mg) was added to one equivalent of BrNI-phen (0.5 mmol, 227 mg) and 20 mL of toluene in a 50 mL round bottom flask. The solution was degassed, put under N<sub>2</sub>, and refluxed while mixing for 1 hour. After cooling, the yellow precipitate was filtered out on a glass frit and washed with 200 mL of toluene. The yellow solid was dried under vacuum overnight and was obtained in 93% yield (353 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  9.46 (ddd, J = 15.3, 5.1, 1.4 Hz, 2H), 8.82 – 8.74 (m, 2H), 8.60 – 8.49 (m, 2H), 8.29 (dd, J = 8.5, 1.4 Hz, 1H), 8.19 (dd, J = 7.8, 3.2 Hz, 1H), 8.12 (s, 1H), 7.99 (ddd, J = 8.6, 7.3, 2.7 Hz, 1H), 7.92 (dd, J = 8.2, 5.2 Hz, 1H), 7.81 (dd, J = 8.5, 5.0 Hz, 1H).

Synthesis of [*Re*(*BrNI-phen*)(*CO*)<sub>3</sub>(*dmap*)](*PF*<sub>6</sub>) (*Re2*). Re(BrNI-phen)(CO)<sub>3</sub>Cl (0.25 mmol, 190 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from solution. The yellow filtrate was added to an excess of dimethylaminopyridine (0.375 mmol, 46 mg) and the solution was then refluxed for an additional 6 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 250 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium hexafluorophosphate solution in water. The yellow solid was dried under vacuum overnight and was obtained in 90% yield (223 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.58 (ddd, J = 12.1, 5.1, 1.3 Hz, 2H), 8.81 (ddd, J = 9.3, 8.6, 1.2 Hz, 2H), 8.72 (ddd, J = 15.2, 7.3, 1.2 Hz, 1H), 8.52 – 8.43 (m, 2H), 8.26 (s, 1H), 8.23 – 8.13 (m, 2H), 8.08 – 7.96 (m, 2H), 7.65 (d, J = 7.4 Hz, 2H), 6.27 (d, J =

7.4 Hz, 2H), 2.91 (d, J = 0.5 Hz, 6H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 844.0316 [M–PF<sub>6</sub>]<sup>+</sup>, calcd ( $C_{34}H_{22}N_5O_5^{185}Re^{79}Br$ ) 844.0334. Anal. Calcd (found) for  $C_{34}H_{22}BrF_6N_5O_5PRe \cdot 0.5H_2O$ : C, 40.81 (40.58); H, 2.32 (2.17); N, 7.00 (6.72). ATR-FTIR: 418, 477, 514, 543, 557, 726, 781, 838, 1234, 1364, 1363, 1589, 1626, 1673, 1713, 1905, 2028 cm<sup>-1</sup>.



**Figure S11**. <sup>1</sup>H NMR spectrum of [Re(BrNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re2**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



**Figure S12**. <sup>1</sup>H NMR spectrum of [Re(BrNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re2**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S13**. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of [Re(BrNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re2**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S14. HRMS spectrum of [Re(BrNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re2).

Synthesis of 6-phenoxy-2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**PONI**). NNI (1 mmol, 332 mg), phenol (5 mmol, 471 mg), and anhydrous potassium carbonate (5 mmol, 675 mg) were heated at 100 °C in anhydrous dimethylformamide (40 mL) for 4 h. Once cool, 40 mL of distilled water was added to solution to precipitate product. The solid was collected on a glass frit and washed with 200 mL of water. The solid was recrystallized by dissolving in hot ethanol and cooling in a freezer. The off-white product was dried under vacuum overnight and was obtained in 86% yield (326 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  8.78 (dd, J = 8.4, 1.2 Hz, 1H), 8.66 (dd, J = 7.3, 1.2 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 8.4, 7.3 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.39 – 7.30 (m, 3H), 7.27 – 7.22 (m, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.3 Hz, 1H), 2.46 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 380.1289 [M+H]<sup>+</sup>, calcd (C<sub>25</sub>H<sub>18</sub>NO<sub>3</sub>) 380.1287. Anal. Calcd

(found) for C<sub>25</sub>H<sub>17</sub>NO<sub>3</sub>·0.1H<sub>2</sub>O: C, 78.77 (78.84); H, 4.55 (4.73); N, 3.67 (3.67). ATR-FTIR: 485, 696, 753, 779, 804, 1136, 1177, 1201, 1236, 1356, 1575, 1660, 1699 cm<sup>-1</sup>.



Figure S15. <sup>1</sup>H NMR spectrum of PONI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S16. <sup>1</sup>H NMR spectrum of PONI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



Figure S17. HRMS spectrum of PONI.

Synthesis of 2-(1,10-phenanthrolin-5-yl)-6-phenoxy-1H-benzo[de]isoquinoline-1,3(2H)-dione (PONI-phen). NNI-phen (1 mmol, 420 mg), phenol (5 mmol, 471 mg), and anhydrous potassium carbonate (5 mmol, 675 mg) were heated at 100 °C in anhydrous dimethylformamide (40 mL) for 4 h. Once cool, 40 mL of distilled water was added to solution to precipitate product. The solid was collected on a glass frit and washed with 200 mL of water. The tan product was dried under vacuum overnight and was obtained in 90% yield (460 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.20 (ddd, J = 17.8, 4.3, 1.7 Hz, 2H), 8.88 (dd, J = 8.4, 1.2 Hz, 1H), 8.73 (dd, J = 7.3, 1.2 Hz, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.36 – 8.31 (m, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.71

(dd, J = 8.1, 4.3 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.40 – 7.33 (m, 1H), 7.28 (dd, J = 8.7, 1.1 Hz, 2H), 7.01 (d, J = 8.3 Hz, 1H).

Synthesis of  $Re(PONI-phen)(CO)_3Cl$ . Pentacarbonylchlororhenium(I) (0.4 mmol, 145 mg) was added to one equivalent of PONI-phen (0.4 mmol, 187 mg) and 20 mL of toluene in a 50 mL round bottom flask. The solution was degassed, put under N<sub>2</sub>, and refluxed while mixing for 1 hour. After cooling, the yellow precipitate was filtered out on a glass frit and washed with 200 mL of toluene. The yellow solid was dried under vacuum overnight and was obtained in 92% yield (284 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.43 (ddd, J = 13.2, 5.1, 1.4 Hz, 2H), 8.92 (d, J = 8.5 Hz, 1H), 8.75 (ddd, J = 13.8, 7.2, 1.2 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.53 (dd, J = 13.7, 8.3 Hz, 1H), 8.37 (dd, J = 8.5, 1.3 Hz, 1H), 8.17 (s, 1H), 7.99 – 7.88 (m, 2H), 7.83 (dd, J = 8.5, 5.0 Hz, 1H), 7.55 (dd, J = 8.5, 7.4 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.01 (dd, J = 8.2, 1.9 Hz, 1H).

*Synthesis of* [ $Re(PONI-phen)(CO)_3(dmap)$ ]( $PF_6$ ) (Re3). Re(PONI-phen)(CO)\_3Cl (0.25 mmol, 193 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from solution. The yellow filtrate was added to an excess of dimethylaminopyridine (2.5 mmol, 305 mg) and the solution was then refluxed for an additional 3 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 250 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium

hexafluorophosphate solution in water. The yellow solid was dried under vacuum overnight and was obtained in 90% yield (226 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>), 9.58 (ddd, *J* = 11.6, 5.2, 1.4 Hz, 2H), 8.94 (dd, J = 8.5, 1.2 Hz, 1H), 8.82 (dd, J = 8.4, 1.4 Hz, 1H), 8.71 (ddd, J = 15.9, 7.3, 1.2 Hz, 1H), 8.56 – 8.44 (m, 2H), 8.24 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.08 – 8.01 (m, 1H), 7.93 (ddd, J = 8.4, 7.3, 4.5 Hz, 1H), 7.65 (dd, J = 7.4, 2.2 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.38 (td, J = 7.4, 1.2 Hz, 1H), 7.29 (dd, J = 7.5, 1.2 Hz, 2H), 7.01 (dd, J = 8.3, 4.4 Hz, 1H), 6.26 (dd, J = 7.3, 5.2 Hz, 2H), 2.91 (s, 3H), 2.90 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 858.1478 [M–PF6]<sup>+</sup>, calcd (C40H<sub>2</sub>7NsO6<sup>185</sup>Re) 858.1491. Anal. Calcd (found) for C40H<sub>2</sub>7F6NsO6PRe·H<sub>2</sub>O: C, 46.97 (47.06); H, 2.86 (2.68); N, 6.85 (6.79). ATR-FTIR: 557, 781, 840, 1206, 1236, 1254, 1356, 1579, 1626, 1671, 1707, 1907, 2028 cm<sup>-1</sup>.



**Figure S18**. <sup>1</sup>H NMR spectrum of [Re(PONI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re3**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



**Figure S19**. <sup>1</sup>H NMR spectrum of [Re(PONI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re3**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S20**. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of [Re(PONI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re3**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S21. HRMS spectrum of [Re(PONI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re3).

Synthesis of 6-(phenylthio)-2-(p-tolyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**PSNI**). NNI (1 mmol, 332 mg), benzenethiol (5 mmol, 563  $\mu$ L), and anhydrous potassium carbonate (5 mmol, 675 mg) were heated at 100 °C in anhydrous dimethylformamide (40 mL) for 4 h. Once cool, 40 mL of distilled water was added to solution to precipitate product. The solid was collected on a glass frit and washed with 200 mL of water. The solid was recrystallized by dissolving in hot ethanol and cooling in a freezer. The yellow product was dried under vacuum overnight and was obtained in 80% yield (317 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  8.73 (dd, J = 8.5, 1.1 Hz, 1H), 8.64 (dd, J = 7.3, 1.1 Hz, 1H), 8.35 (d, J = 7.9 Hz, 1H), 7.84 (dd, J = 8.5, 7.3 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.51 – 7.45 (m, 3H), 7.39 – 7.32 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 396.1058 [M+H]<sup>+</sup>, calcd (C<sub>2</sub>sH<sub>18</sub>NO<sub>2</sub>S) 396.1058. Anal. Calcd (found) for

C<sub>25</sub>H<sub>17</sub>NO<sub>2</sub>S: C, 75.93 (75.66); H, 4.33 (4.56); N, 3.54 (3.54). ATR-FTIR: 445, 516, 685, 747, 777, 810, 904, 1134, 1175, 1185, 1230, 1346, 1361, 1507, 1562, 1581, 1656, 1697 cm<sup>-1</sup>.



Figure S22. <sup>1</sup>H NMR spectrum of PSNI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S23. <sup>1</sup>H NMR spectrum of PSNI in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



Figure S24. HRMS spectrum of PSNI.

Synthesis of 2-(1,10-phenanthrolin-5-yl)-6-(phenylthio)-1H-benzo[de]isoquinoline-1,3(2H)dione (PSNI-phen). NNI-phen (1 mmol, 420 mg), phenol (5 mmol, 563 µL), and anhydrous potassium carbonate (5 mmol, 675 mg) were heated at 100 °C in anhydrous dimethylformamide (40 mL) for 4 h. Once cool, 40 mL of distilled water was added to solution to precipitate product. The solid was collected on a glass frit and washed with 500 mL of water. The tan product was dried under vacuum overnight and was obtained in 66% yield (321 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.22 (dd, J = 4.4, 1.8 Hz, 1H), 9.18 (dd, J = 4.3, 1.7 Hz, 1H), 8.83 (dd, J = 8.5, 1.1 Hz, 1H), 8.71 (dd, J = 7.3, 1.1 Hz, 1H), 8.40 (d, J = 7.9 Hz, 1H), 8.36 – 8.30 (m, 1H), 8.04 (dd, J = 8.3, 1.7 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.71 (dd, J = 8.0, 4.4 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.55 – 7.48 (m, 3H), 7.36 (d, J = 7.9 Hz, 1H).

Synthesis of  $Re(PSNI-phen)(CO)_3Cl$ . Pentacarbonylchlororhenium(I) (0.5 mmol, 181 mg) was added to one equivalent of PSNI-phen (0.5 mmol, 242 mg) and 20 mL of toluene in a 50 mL round bottom flask. The solution was degassed, put under N<sub>2</sub>, and refluxed while mixing for 1 hour. After cooling, the yellow precipitate was filtered out on a glass frit and washed with 200 mL of toluene. The yellow solid was dried under vacuum overnight and was obtained in 94% yield (369 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  9.44 (ddd, J = 14.3, 5.1, 1.4 Hz, 2H), 8.84 (ddd, J = 8.5, 3.4, 1.1 Hz, 1H), 8.75 (ddd, J = 12.0, 7.3, 1.1 Hz, 1H), 8.56 (dd, J = 8.2, 1.4 Hz, 1H), 8.43 (dd, J = 10.4, 8.0 Hz, 1H), 8.28 (dd, J = 8.5, 1.3 Hz, 1H), 8.10 (s, 1H), 7.96 – 7.86 (m, 2H), 7.78 (dd, J = 8.4, 5.1 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.56 – 7.50 (m, 3H), 7.28 (dd, J = 8.0, 2.6 Hz, 1H).

*Synthesis of* [ $Re(PSNI-phen)(CO)_3(dmap)$ ]( $PF_6$ ) (Re4). Re(PSNI-phen)(CO)\_3CI (0.25 mmol, 197 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from solution. The yellow filtrate was added to an excess of dimethylaminopyridine (2.5 mmol, 305 mg) and the solution was then refluxed for an additional 5 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 250 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium

hexafluorophosphate solution in water. The yellow solid was dried under vacuum overnight and was obtained in 96% yield (245 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.57 (ddd, J = 12.6, 5.1, 1.4 Hz, 2H), 8.84 (ddd, J = 24.3, 8.5, 1.3 Hz, 2H), 8.70 (ddd, J = 16.3, 7.3, 1.1 Hz, 1H), 8.48 (dd, J = 8.5, 1.3 Hz, 1H), 8.36 (dd, J = 15.7, 8.0 Hz, 1H), 8.23 (s, 1H), 8.16 (dd, J = 8.3, 5.2 Hz, 1H), 8.04 (dd, J = 8.5, 5.1 Hz, 1H), 7.93 (ddd, J = 8.5, 7.4, 4.7 Hz, 1H), 7.67 – 7.62 (m, 4H), 7.56 – 7.52 (m, 3H), 7.31 (dd, J = 8.0, 5.0 Hz, 1H), 6.26 (td, J = 5.5, 1.6 Hz, 2H), 2.91 (s, 3H), 2.89 (s, 3H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 874.1242 [M–PF6]<sup>+</sup>, calcd (C<sub>40</sub>H<sub>27</sub>NsO<sub>5</sub>S<sup>185</sup>Re) 874.1262. Anal. Calcd (found) for C<sub>40</sub>H<sub>27</sub>F<sub>6</sub>N<sub>5</sub>O<sub>5</sub>PReS: C, 47.06 (46.98); H, 2.67 (2.68); N, 6.86 (6.78). ATR-FTIR: 557, 728, 751, 779, 838, 1234, 1363, 1585, 1626, 1671, 1709, 1905, 2028 cm<sup>-1</sup>.



**Figure S25**. <sup>1</sup>H NMR spectrum of [Re(PSNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re4**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



**Figure S26**. <sup>1</sup>H NMR spectrum of [Re(PSNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re4**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S27**. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of [Re(PSNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re4**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S28. HRMS spectrum of [Re(PSNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re4).

*Synthesis of* [ $Re(PNI-phen)(CO)_3(dmap)$ ]( $PF_6$ ) (Re5). Re(PNI-phen)(CO)\_3Cl (0.25 mmol, 191 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from solution. The orange filtrate was added to an excess of dimethylaminopyridine (2.5 mmol, 305 mg) and the solution was then refluxed for an additional 3 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 250 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium

hexafluorophosphate solution in water. The orange solid was dried under vacuum overnight and was obtained in 96% yield (240 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.56 (ddd, J = 13.1, 5.1, 1.4 Hz, 2H), 8.80 (dd, J = 8.3, 1.4 Hz, 1H), 8.66 – 8.44 (m, 4H), 8.22 (s, 1H), 8.14 (dd, J = 8.3, 5.2 Hz, 1H), 8.02 (dd, J = 8.5, 5.1 Hz, 1H), 7.79 (ddd, J = 8.5, 7.3, 5.3 Hz, 1H), 7.64 (d, J = 7.4 Hz, 2H), 7.27 (dd, J = 8.2, 6.1 Hz, 1H), 6.26 (d, J = 7.4 Hz, 2H), 3.36 (m, J = 5.4 Hz, 4H), 2.91 (s, 6H), 1.92 (m, J = 10.7 Hz, 4H), 1.78 (m, 2H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 849.1945 [M–PF<sub>6</sub>]<sup>+</sup>, calcd (C<sub>39</sub>H<sub>32</sub>N<sub>6</sub>O<sub>5</sub><sup>185</sup>Re) 849.1964. Anal. Calcd (found) for C<sub>39</sub>H<sub>32</sub>F<sub>6</sub>N<sub>6</sub>O<sub>5</sub>PRe·H<sub>2</sub>O: C, 46.20 (46.17); H, 3.38 (3.16); N, 8.29 (8.10). ATR-FTIR: 557, 781, 840, 1232, 1365, 1583, 1626, 1664, 1701, 1909, 2028 cm<sup>-1</sup>.



**Figure S29**. <sup>1</sup>H NMR spectrum of [Re(PNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re5**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



**Figure S30**. <sup>1</sup>H NMR spectrum of [Re(PNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re5**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S31**. <sup>1</sup>H NMR spectrum of [Re(PNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re5**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aliphatic region.



**Figure S32**. <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of [Re(PNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re5**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz).



Figure S33. HRMS spectrum of [Re(PNI-phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re5).

*Synthesis of* [ $Re(phen)(CO)_3(dmap)$ ]( $PF_6$ ) (Re6). Re(phen)(CO)\_3Cl (0.25 mmol, 122 mg) and silver triflate (0.26 mmol, 67 mg) were added to 100 mL round bottom flask along with 50 mL of absolute ethanol. The solution was covered (dark), deaerated, put under N<sub>2</sub>, and refluxed for 6 hours. Once cool, the solution was filtered through celite on a glass frit to remove AgCl from solution. The yellow filtrate was added to an excess of dimethylaminopyridine (2.5 mmol, 305 mg) and the solution was then refluxed for an additional 3 hours. The solvent volume was reduced to approximately 10 mL, followed by a dropwise addition of an ammonium hexafluorophosphate solution in water (1.0 g in 10 mL) to precipitate the product. The solid was collected on a glass frit and washed with 250 mL of distilled water. The solid was recrystallized by dissolving in hot methanol and slowly precipitating the solid with a slow addition of ammonium

hexafluorophosphate solution in water. The orange solid was dried under vacuum overnight and was obtained in 83% yield (148 mg). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  9.51 (dd, J = 5.1, 1.4 Hz, 2H), 8.79 (dd, J = 8.3, 1.4 Hz, 2H), 8.17 (s, 2H), 8.10 (dd, J = 8.3, 5.1 Hz, 2H), 7.53 (d, J = 7.4 Hz, 2H), 6.19 (d, J = 7.4 Hz, 2H), 2.86 (s, 6H). MS [HR-ESI (CH<sub>2</sub>Cl<sub>2</sub>) m/z] 571.0909 [M–PF<sub>6</sub>]<sup>+</sup>, calcd (C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub><sup>185</sup>Re) 571.0908. Anal. Calcd (found) for C<sub>22</sub>H<sub>18</sub>F<sub>6</sub>N<sub>4</sub>O<sub>3</sub>PRe·0.5H<sub>2</sub>O: C, 36.37 (36.52); H, 2.64 (2.42); N, 7.71 (7.59). ATR-FTIR: 557, 724, 836, 1626, 1897, 1919, 2025 cm<sup>-1</sup>.



**Figure S34**. <sup>1</sup>H NMR spectrum of [Re(phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re6**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



**Figure S35**. <sup>1</sup>H NMR spectrum of [Re(phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (**Re6**) in CD<sub>2</sub>Cl<sub>2</sub> (400 MHz) with zoomed in aromatic region.



Figure S36. HRMS spectrum of [Re(phen)(CO)<sub>3</sub>(dmap)](PF<sub>6</sub>) (Re6).



Figure S37. ATR-FTIR spectra of NI, BrNI, PONI, PSNI, and PNI.


Figure S38. ATR-FTIR spectra of Re1-Re6.

## 2. Additional Optical Spectra



Figure S39. (a) Electronic spectra of NI, BrNI, PONI, PSNI, and PNI in THF. (b) Electronic spectra of Re1-Re6 in THF.



**Figure S40**. (a) Additive combination of electronic spectra between organic chromophore model and Re(I) model in ACN. (b) Electronic spectra of **Re1-Re6** in ACN.



**Figure S41**. (a) Additive combination of electronic spectra between organic chromophore model and Re(I) model in THF. (b) Electronic spectra of **Re1-Re6** in THF.



Figure S42. Photoluminescence spectra of NI, BrNI, PONI, PSNI, PNI, and Re1-Re6 in THF.



Figure S43. Excitation spectra of NI in ACN monitored at shortwave (left) and longwave (right) emission maxima.



**Figure S44**. Excitation spectra of BrNI in ACN monitored at shortwave (left) and longwave (right) emission maxima.



**Figure S45**. Photoluminescence decay of **Re1** at 600 nm in ACN (left) and THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S46**. Photoluminescence decay of **Re2** at 600 nm in ACN (left) and THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S47**. Photoluminescence Decay of **Re3** at 600 nm in ACN (left) and 590 nm in THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S48**. Photoluminescence decay of **Re6** at 600 nm in ACN (left) and THF (right). Excited at 410 nm (3 mJ/pulse).



**Figure S49**. Time-resolved photoluminescence emission spectra of **Re1** (A), **Re2** (B), **Re3** (C), **Re4** (D), and **Re5** (E) at specified times after a 7 ns, 350 nm (**Re1-Re3**) and 400 nm (**Re4** and **Re5**) laser pulse in deaerated ACN.



**Figure S50**. Time-resolved 77 K photoluminescence emission spectra of **NI**, **BrNI**, **PONI**, **PSNI**, and **PNI** at 25 ms after a 7 ns, 400 nm laser pulse in 2-methyl THF with 10% ethyl iodide.



## 3. Additional Transient Absorption Spectra

**Figure S51**. Excited-state absorption difference spectra of **NI** in ACN during short delay times (A) and long delay times (B) following 350 nm pulsed excitation (105 fs fwhm).



**Figure S52**. Excited-state absorption difference spectra of **BrNI** in ACN during short delay times (A) and long delay times (B) following 350 nm pulsed excitation (105 fs fwhm).



**Figure S53**. Excited-state absorption difference spectra of **Re1** in ACN during short delay times (A) and long delay times (B) following 400 nm pulsed excitation (105 fs fwhm).



**Figure S54**. Ultrafast transient absorption kinetic data of **Re1** in ACN following 350 nm pulsed excitation. (A) Single wavelength kinetic analysis at 470 nm. (B) Single wavelength kinetic analysis at 370 nm. (C) Single wavelength kinetic analysis at 470 nm.



**Figure S55**. Global fit spectral analysis of ultrafast transient absorption data of Re(NIphen)(CO)<sub>3</sub>Cl in THF (A), **Re1** in THF (B), and **Re1** in ACN (C) following 350 nm pulsed excitation.



**Figure S56**. Excited-state absorption difference spectra of **Re2** in ACN during short delay times (A) and long delay times (B) following 350 nm pulsed excitation (105 fs fwhm).



**Figure S57**. Ultrafast transient absorption kinetic data of **Re2** in ACN following 350 nm pulsed excitation. (A) Single wavelength kinetic analysis at 485 nm. (B) Single wavelength kinetic analysis at 375 nm. (C) Single wavelength kinetic analysis at 485 nm.



**Figure S58**. Global fit spectral analysis of ultrafast transient absorption data Re(BrNIphen)(CO)<sub>3</sub>Cl in THF (A), **Re2** in THF (B), and **Re2** in ACN (C) following 350 nm pulsed excitation.



**Figure S59**. Excited-state absorption difference spectra of **PONI** in ACN during short delay times (A) and long delay times (B) following 350 nm pulsed excitation (105 fs fwhm).



**Figure S60**. Ultrafast transient absorption kinetic data of **Re3** in ACN following 350 nm pulsed excitation. (A) Single wavelength kinetic analysis at 370 nm. (B) Single wavelength kinetic analysis at 425 nm. (C) Single wavelength kinetic analysis at 500 nm. (D) Single wavelength kinetic analysis at 475 nm.



**Figure S61**. Global fit spectral analysis of ultrafast transient absorption data of Re(PONIphen)(CO)<sub>3</sub>Cl in THF (A), **Re3** in THF (B), and **Re3** in ACN (C) following 350 nm pulsed excitation.



**Figure S62**. Excited-state absorption difference spectra of **PSNI** in ACN during short delay times (A) and long delay times (B) following 400 nm pulsed excitation (105 fs fwhm).



**Figure S63**. Ultrafast transient absorption kinetic data of **Re4** in ACN following 400 nm pulsed excitation. Single wavelength kinetic analysis at 450 nm (A), 520 nm (B), and 615 (C) at short time after the laser pulse. Single wavelength kinetic analysis at 390 nm (D), 430 nm (E), and 650 (F) at longer time after the laser pulse.



**Figure S64**. Global fit spectral analysis of ultrafast transient absorption data of Re(PSNIphen)(CO)<sub>3</sub>Cl in THF (A), **Re4** in THF (B), and **Re4** in ACN (C) following 400 nm pulsed excitation.



**Figure S65**. Excited-state absorption difference spectra of **PNI** in ACN during short delay times (A) and long delay times (B) following 400 nm pulsed excitation (105 fs fwhm).



**Figure S66**. Ultrafast transient absorption kinetic data of **Re5** in ACN following 400 nm pulsed excitation. Single wavelength kinetic analysis at 425 nm (A) and 550 nm (B) at short time after the laser pulse. Single wavelength kinetic analysis at 415 nm (C) and 475 nm (D) at longer time after the laser pulse.



**Figure S67**. Global fit spectral analysis of ultrafast transient absorption data of Re(PNIphen)(CO)<sub>3</sub>Cl in THF (A), **Re5** in THF (B), and **Re5** in ACN (C) following 400 nm pulsed excitation.



**Figure S68**. Excited-state absorption difference spectra of **Re6** in ACN following 400 nm pulsed excitation (105 fs fwhm).



**Figure S69**. Ultrafast transient absorption kinetic data of **Re6** in ACN following 400 nm pulsed excitation.

Molecule	Solvent	τ <sub>1</sub> (ps)	τ <sub>2</sub> (ps)	τ₃ (ps)	τ4 (ns)
Re(NI-phen)(CO)₃Cl	THF	0.04 ± 0.05	0.37 ± 0.06		
[Re(NI-phen)(CO)₃(dmap)](PF₀)	THF	0.07 ± 0.03	0.42 ± 0.05	43.5 ± 6.8	4.4 ± 0.6
	ACN	$0.40 \pm 0.03$		44.0 ± 6.5	5.4 ± 1.0
Re(BrNI-phen)(CO)₃Cl	THF	0.36 ± 0.1			
[Re(BrNI-phen)(CO)₃(dmap)](PF <sub>6</sub> )	THF		0.53 ± 0.15	28 ± 16	5.5 ± 3.5
	ACN	0.37 ± 0.02		51.1 ± 9.8	3.8 ± 0.5
Re(PONI-phen)(CO)₃Cl	THF	0.64 ± 0.15			3.8 ± 4.0
[Re(PONI-phen)(CO)₃(dmap)](PF <sub>6</sub> )	THF		1.2 ± 0.2	27 ± 12	5.8 ± 1.5
	ACN	$0.17 \pm 0.04$	$1.6 \pm 0.2$	28.1 ± 5.2	$5.4 \pm 0.6$
Re(PSNI-phen)(CO)₃Cl	THF	0.12 ± 0.05	1.3 ± 0.3	30.3 ± 2.8	17.8 ± 17
[Re(PSNI-phen)(CO)₃(dmap)](PF <sub>6</sub> )	THF		1.8 ± 0.3	43.7 ± 4.4	3.1 ± 1.0
	ACN		2.4 ± 0.3	73.1 ± 4.3	2.9 ± 1.0
Re(PNI-phen)(CO)₃Cl	THF	0.16 ± 0.05	$2.4 \pm 0.4$	48.2 ± 0.9	9.2 ± 1.7
[Re(PNI-phen)(CO)₃(dmap)](PF <sub>6</sub> )	THF		49.8 ± 1.3	394 ± 62	3.9 ± 3.8
	ACN	0.51 ± 0.05	22.7 ± 4.9	66.2 ± 21	$2.1 \pm 0.4$

 Table S1. Summary of time constants from UFTA global fit analysis.



**Figure S70**. Excited-state absorption difference spectra of **NI** (A), **BrNI** (B), **PONI** (C), and **PSNI** (D) in ACN following 350 nm pulsed excitation (3 mJ/pulse, 7 ns fwhm).



Figure S71. Transient absorption decay of NI in ACN. Excited at 355 nm (3 mJ/pulse).



Figure S72. Transient absorption decay of BrNI in ACN. Excited at 355 nm (3 mJ/pulse).



Figure S73. Transient absorption decay of PONI in ACN. Excited at 355 nm (3 mJ/pulse).



Figure S74. Transient absorption decay of PSNI in ACN. Excited at 355 nm (3 mJ/pulse).



**Figure S75**. Excited-state absorption difference spectra of **Re1** (A), **Re2** (B), **Re3** (C), **Re4** (D), and **Re5** (E) in THF. **Re1-3** were excited using a Continuum Minilite with 355 nm pulsed excitation (3.4 mJ/pulse, 5 ns fwhm). **Re4-5** were excited using the OPOTEK with 410 nm pulsed excitation (3 mJ/pulse, 7 ns fwhm).



**Figure S76**. Transient absorption decay of **Re1** in ACN (left) and THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S77**. Transient absorption decay of **Re2** in ACN (left) and THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S78**. Transient absorption decay of **Re3** in ACN (left) and THF (right). Excited at 355 nm (3 mJ/pulse).



**Figure S79**. Transient absorption decay of **Re4** in ACN (left) and THF (right). Excited at 410 nm (3 mJ/pulse).


**Figure S80**. Transient absorption decay of **Re5** in ACN (left) and THF (right). Excited at 410 nm (3 mJ/pulse).



**Figure S81**. Transient absorption decay of **Re6** in ACN (left) and THF (right). Excited at 410 nm (3 mJ/pulse)

## 4. Additional DFT Results

**Table S2**. Wavelength, energies, and oscillator strength (*f*) for selected  $S_0 \rightarrow S_n$  excitations as determined via TDDFT at the level of theory specified below. Experimental UV/Vis data obtained in acetonitrile at room temperature.

Molecules	$\lambda_{abs max}/nm, eV$ ( $\epsilon/M^{-1}cm^{-1}$ )	B3LYP/Def2-SVP $S_0 \rightarrow S_1/nm, eV(f)$ $S_0 \rightarrow S_2/nm, eV(f)$	M06/Def2-SVP $S_0 \rightarrow S_1/nm$ , eV (f) $S_0 \rightarrow S_2/nm$ , eV (f)	CAM- B3LYP/Def2-SVP $S_0 \rightarrow S_1/nm, eV(f)$ $S_0 \rightarrow S_2/nm, eV(f)$
NI	332, 3.73	342, 3.63 (0.0000)	334, 3.71 (0.2919)	304, 4.08 (0.3548)
	(14200)	337, 3.68 (0.2827)	325, 3.81 (0.0001)	285, 4.35 (0.0536)
BrNI	340, 3.65	353, 3.51 (0.1169)	348, 3.56 (0.3620)	314, 3.95 (0.4364)
	(17100)	352, 3.52 (0.2273)	336, 3.69 (0.0011)	286, 4.34 (0.0417)
PONI	359, 3.45	361, 3.43 (0.3693)	353, 3.51 (0.3891)	321, 3.86 (0.4912)
	(15601)	334, 3.71 (0.0000)	318, 3.90 (0.0013)	281, 4.41 (0.0097)
PSNI	384, 3.23	445, 2.79 (0.0696)	426, 2.91 (0.1021)	340, 3.65 (0.2164)
	(14700)	355, 3.49 (0.0000)	339, 3.66 (0.2885)	302, 4.11 (0.2794)
PNI	407, 3.05	423, 2.93 (0.3296)	403, 3.08 (0.3567)	359, 3.45 (0.4645)
	(11300)	331, 3.75 (0.0001)	316, 3.92 (0.0013)	288, 4.31 (0.0107)

Molecules	λ <sub>em</sub> /nm, eV (at 77 K)	B3LYP/Def2- SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$ $S_0 \rightarrow T_3/nm, eV$	M06/Def2-SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$ $S_0 \rightarrow T_n/nm, eV$	CAM-B3LYP/Def2- SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$ $S_0 \rightarrow T_n/nm, eV$
NI	538, 2.30	536, 2.31 372, 3.33 357, 3.47	535, 2.32 368, 3.37 T <sub>4</sub> : 333, 3.72	549, 2.26 355, 3.49 T <sub>5</sub> : 304, 4.08
BrNI	553, 2.24	554, 2.24 368, 3.37 365, 3.40	556, 2.23 365, 4.30 T <sub>5</sub> : 347, 3.57	567, 2.19 355, 3.49 T <sub>5</sub> : 307, 4.04
PONI	547, 2.27	546, 2.27 361, 3.43 350, 3.54	536, 2.31 356, 3.48 T <sub>6</sub> : 325, 3.81	550, 2.25 355, 3.49 T <sub>6</sub> : 299, 4.15
PSNI	579, 2.14	562, 2.21 447, 2.77 375, 3.31	568, 2.18 428, 2.90 T <sub>3</sub> : 370, 3.35	567, 2.19 369, 3.36 T <sub>3</sub> : 363, 3.42
PNI	605, 2.05	605, 2.05 403, 3.08 354, 3.50	577, 2.15 390, 3.18 T <sub>3</sub> : 351, 3.53	585, 2.12 376, 3.30 T <sub>3</sub> : 355, 3.49

**Table S3**. Wavelength and energies for selected  $S_0 \rightarrow T_n$  excitations as determined via TDDFT at the level of theory specified below. Experimental photoluminescence data obtained in 2-methyltetrahydrofuran at 77 K.



**Figure S82**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **NI** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S83**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **BrNI** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S84**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **PONI** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S85**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **PSNI** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S86**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **PNI** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.

Molecules	$\lambda_{abs max}/nm,$ eV ( $\epsilon/M^{-1}cm^{-1}$ )	B3LYP/Def2-SVP $S_0 \rightarrow S_1/nm, eV(f)$ $S_0 \rightarrow S_2/nm, eV(f)$ $S_0 \rightarrow S_n/nm, eV(f)$	M06/Def2-SVP $S_0 \rightarrow S_1/nm, eV(f)$ $S_0 \rightarrow S_2/nm, eV(f)$ $S_0 \rightarrow S_n/nm, eV(f)$	CAM- B3LYP/Def2-SVP $S_0 \rightarrow S_1/nm, eV(f)$ $S_0 \rightarrow S_2/nm, eV(f)$ $S_0 \rightarrow S_n/nm, eV(f)$
Re1	334, 3.71 (20400)	449, 2.76 (0.0412) 420, 2.95 (0.0056) 87: 359, 3.45 (0.1384)	415, 2.99 (0.0615) 390, 3.44 (0.0013) 87: 341, 3.64 (0.1967)	339, 3.66 (0.1305) 329, 3.77 (0.0021) S4: 306, 4.05 (0.4089)
Re2	343, 3.61 (23200)	450, 2.76 (0.0424) 423, 2.93 (0.0038) 87: 360, 3.44 (0.2752)	416, 2.98 (0.0646) 391, 3.17 (0.0011) 87: 351, 3.53 (0.4580)	339, 3.66 (0.1437) 330, 3.76 (0.0034) S <sub>3</sub> : 316, 3.92 (0.5027)
Re3	364, 3.41 (21600)	448, 2.77 (0.0442) 419, 2.96 (0.0054) S9: 365, 3.40 (0.4800)	415, 2.99 (0.0663) 390, 3.44 (0.0020) \$5: 357, 3.47 (0.2083)	339, 3.66 (0.1735) 329, 3.77 (0.0060) S <sub>3</sub> : 324, 3.83 (0.5314)
Re4	392, 3.16 (20700)	459, 2.70 (0.0946) 450, 2.76 (0.0329) S11: 359, 3.45 (0.1158)	438, 2.83 (0.1282) 415, 2.99 (0.0574) S10: 342, 3.63 (0.4100)	348, 3.56 (0.2763) 339, 3.66 (0.0918)
Re5	415, 2.99 (15800)	461, 2.69 (0.0004) 447, 2.77 (0.0666) S4: 430, 2.88 (0.3384)	414, 2.99 (0.1843) 409, 3.03 (0.2391)	365, 3.40 (0.5691) 338, 3.67 (0.0901)
Re6	368, 3.37 (3160)	438, 2.83 (0.0359) 402, 3.08 (0.0050)	405, 3.06 (0.0536) 383, 3.24 (0.0011)	334, 3.71 (0.1037) 325, 3.81 (0.0015)

**Table S4**. Wavelength, energies, and oscillator strength (*f*) for selected  $S_0 \rightarrow S_n$  excitations as determined via TDDFT at the level of theory specified below. Experimental UV/Vis data obtained in acetonitrile at room temperature.

Molecules	$\lambda_{em}$ /nm, ev (at 77 K) <sup>[a]</sup>	B3LYP/Def2-SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$	M06/Def2-SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$	CAM- B3LYP/Def2-SVP $S_0 \rightarrow T_1/nm, eV$ $S_0 \rightarrow T_2/nm, eV$
Re1	536, 2.31	538, 2.30	536, 2.31	551, 2.25
	512, 2.42	470, 2.64	465, 2.67	466, 2.66
Re2	555, 2.23	557, 2.23	557, 2.23	568, 2.18
	516, 2.40	471, 2.63	464, 2.67	466, 2.66
Re3	546, 2.27	549, 2.26	536, 2.31	551, 2.25
	514, 2.41	470, 2.64	465, 2.67	467, 2.65
Re4	577, 2.15	570, 2.18	573, 2.16	570, 2.18
	516, 2.40	471, 2.63	465, 2.67	466, 2.66
Re5	595, 2.08	614, 2.02	581, 2.13	590, 2.10
	512, 2.42	469, 2.64	464, 2.67	466, 2.66
Re6	507, 2.45	459, 2.70	454, 2.73	460, 2.70

**Table S5**. Wavelength and energies for selected  $S_0 \rightarrow T_n$  excitations as determined via TDDFT at the level of theory specified below. Experimental photoluminescence data obtained in 2-methyltetrahydrofuran at 77 K.

<sup>[a]</sup> Two emission bands corresponding to the LC excited state localized on the NI chromophore (black) and MLCT excited state localized on the Re(I) chromophore (blue) were observed.



**Figure S87**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re1** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S88**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re2** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S89**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re3** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S90**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re4** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S91**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re5** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.



**Figure S92**. Natural transition orbitals for selected  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  excitations of **Re6** determined at the M06/Def2-SVP (left) and CAM-B3LYP/Def2-SVP (right) levels of theory;  $\lambda$  is the fraction of the hole–particle contribution to the excitation.