Supporting Information

Probing Recombination Mechanism and Realization of Marcus Normal Region Behavior in DSSCs Employing Cobalt Electrolytes and Triphenylamine Dyes

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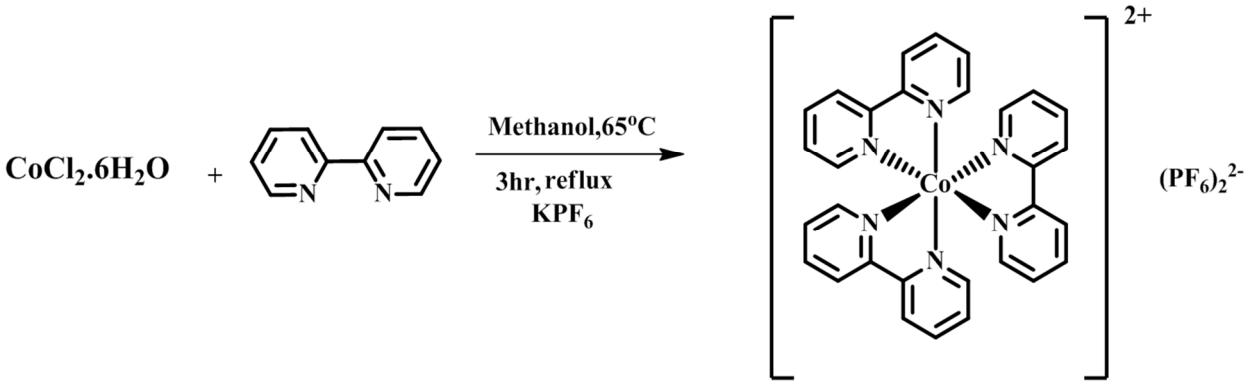
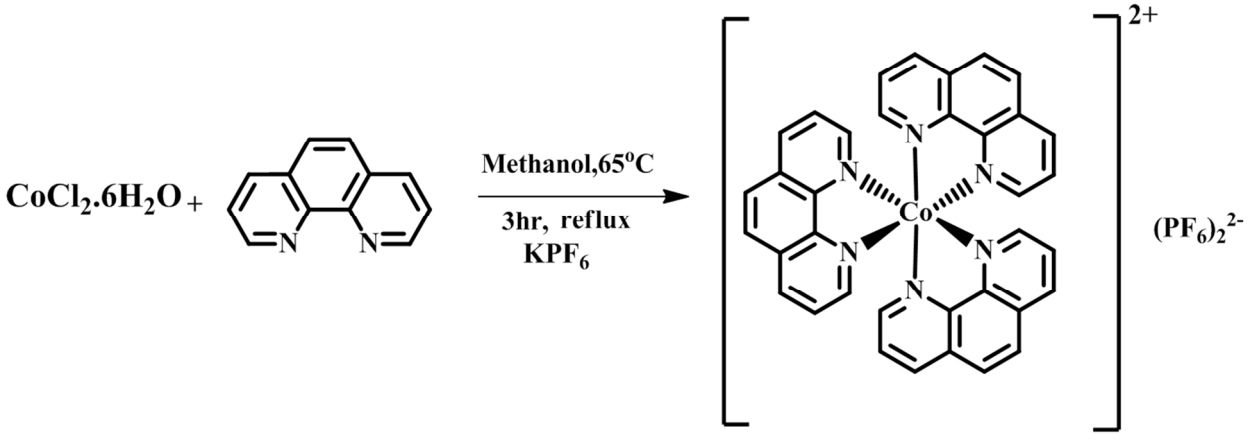
General procedure for the synthesis of cobalt complexes

1eq. of $CoCl_2$.$6H_2O$ and 3eq. of polypyridine ligand were dissolved in minimal amount of methanol, and the solution was stirred at 65 °C and reflux for 3-4 hours. An excess of potassium hexafluorophosphate was then added to the solution to precipitate the compound that was filtered, washed with methanol and ethanol, dried under vaccum and used without purification.



$[Co(bpy)_3](PF_6)_2$

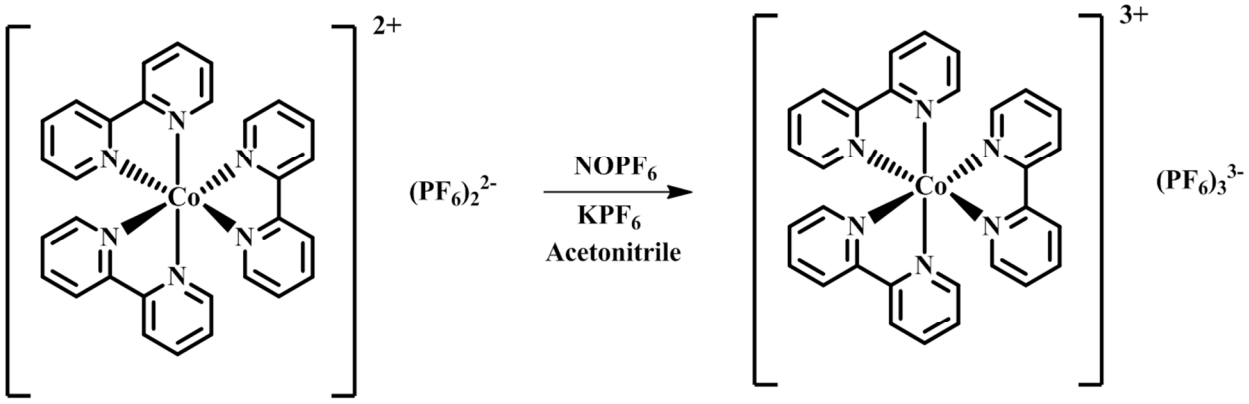


$[Co(phen)_3](PF_6)_2$

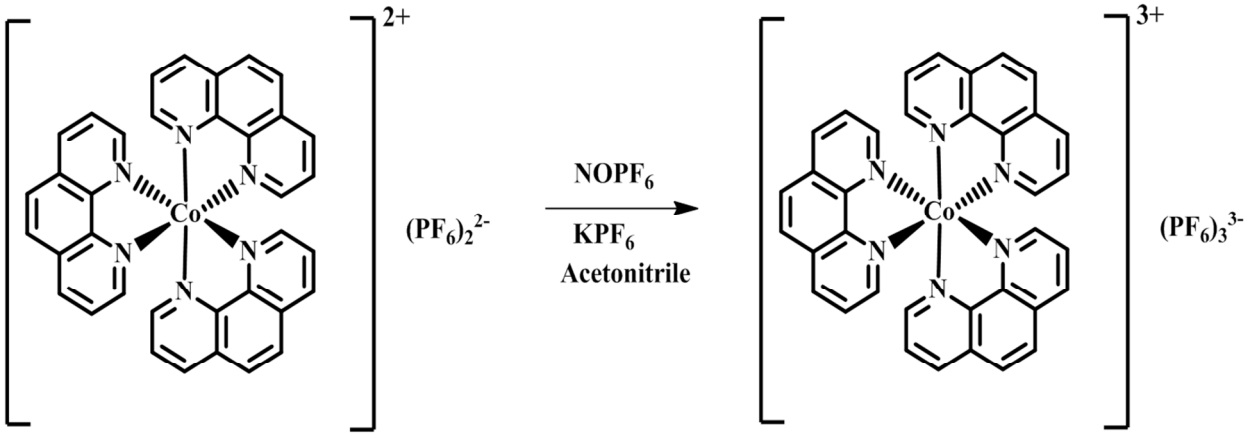
General procedure for the oxidation of cobalt (II) to cobalt (III)

Oxidation of cobalt (II) complexes was performed by adding a slight excess of $NOPF_6$ to dry acetonitrile solution of the complex and then by removing the acetonitrile solution by rotary evaporation. The complex was then re-dissolved in acetonitrile and a large amount of KPF_6 was added to the solution. The final product was precipitated with diethyl ether, filtered, dried under vaccum and used without further purification. It is characterized using ^1H NMR and COSY shown in Figure S1,S2,S3 and S4

All the synthesis was carried out using the already reported procedures.[1,2,3,4]



$[Co(bpy)_3](PF_6)_2$ **$[Co(bpy)_3](PF_6)_3$**



$[Co(phen)_3](PF_6)_2$ **$[Co(phen)_3](PF_6)_3$**

Synthesis of cobalt (II) trisbipyridine hexafluorophosphate $[Co(bpy)_3](PF_6)_2$ and cobalt (III) trisbipyridine hexafluorophosphate $[Co(bpy)_3](PF_6)_3$

$[Co(bpy)_3](PF_6)_2$: 3g (0.0126moles) of cobalt dichloride hexahydrate, 5.9g (0.0378moles) of 2,2′-bipyridine excess amount of potassium hexafluorophosphate. Yield-71.83%

$[Co(bpy)_3](PF_6)_3$: 2g of $[Co(bpy)_3](PF_6)_2$, Catalytic amount of $NOPF_6$, excess amount of potassium hexafluorophosphate. Yield-98%

^1H NMR (CD_3CN, 500MHz): δ 6 (d,1H), 7.739-7.709 (m, 1H), 8.484-8.450 (m, 1H), 8.6 (dd, 1H, J_1=1, J_2=8) ppm.

Synthesis of cobalt (II) trisphenanthroline hexafluorophosphate $[Co(phen)_3](PF_6)_2$ and cobalt (III) trisphenanthroline hexafluorophosphate $[Co(phen)_3](PF_6)_3$

For $[Co(phen)_3](PF_6)_2$: 2g (0.00845 moles) of cobalt dichloride hexahydrate 4.99 g (0.0252 moles) phenanthroline, excess amount of potassium hexafluorophosphate. Yield-90.33%

For $[Co(phen)_3](PF_6)_3$: 1g of $[Co(phen)_3](PF_6)_2$, Catalytic amount of $NOPF_6$, excess amount of potassium hexafluorophosphate. Yield-22%

^1H NMR (CD_3CN, 500 MHz): δ 5.5 (d, 1H), 7.8 (dd, 1H, J_1=5.5, J_2=8), 8.4 (s, 1H), 9 (dd, 1H, J_1=1, J_2=8.5) ppm.

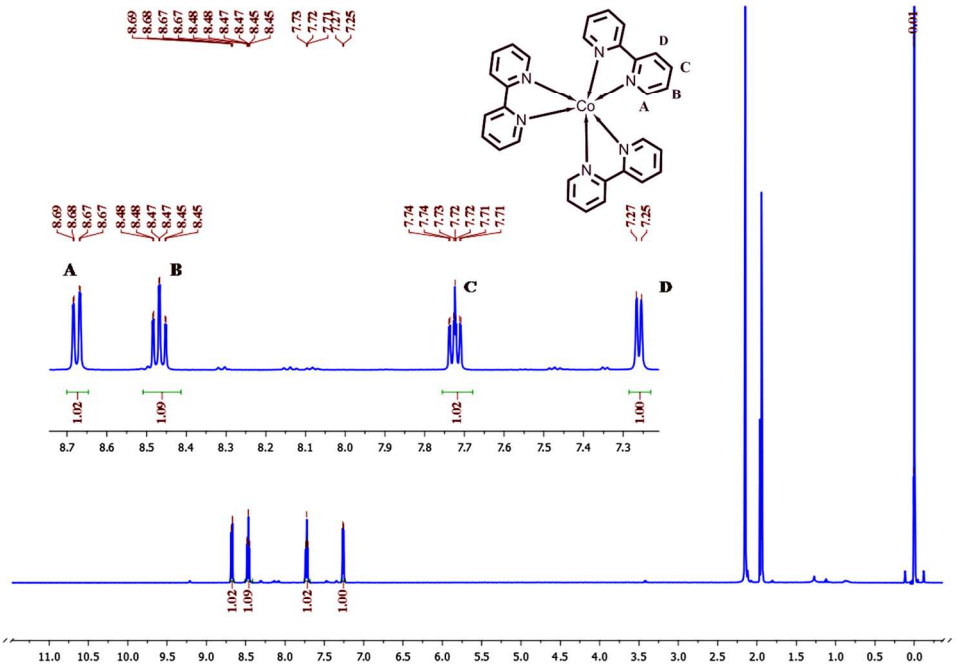


Figure S1. ^{1}HNMR of $[Co(bpy)_3](PF_6)_3$.

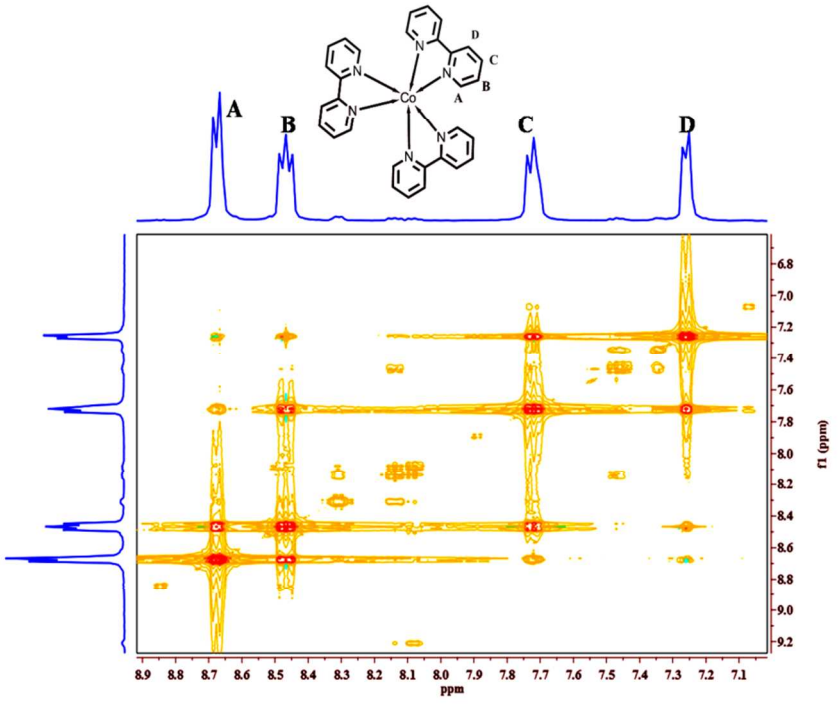


Figure S2. COSY of $[Co(bpy)_3](PF_6)_3$.

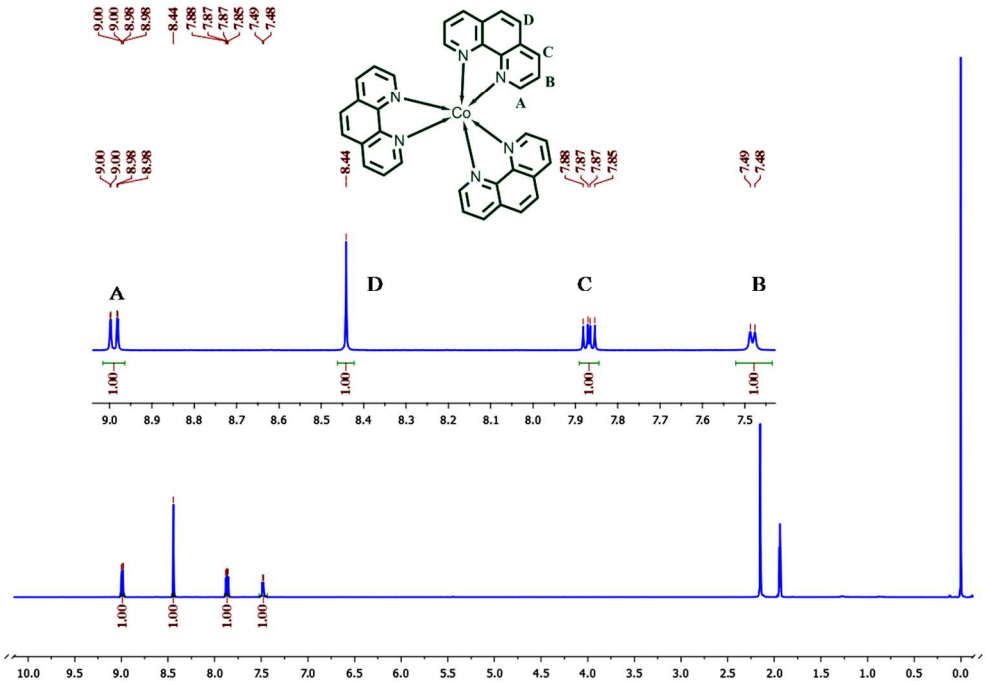


Figure S3. ^{1}H NMR of $[Co(phen)_3](PF_6)_3$.

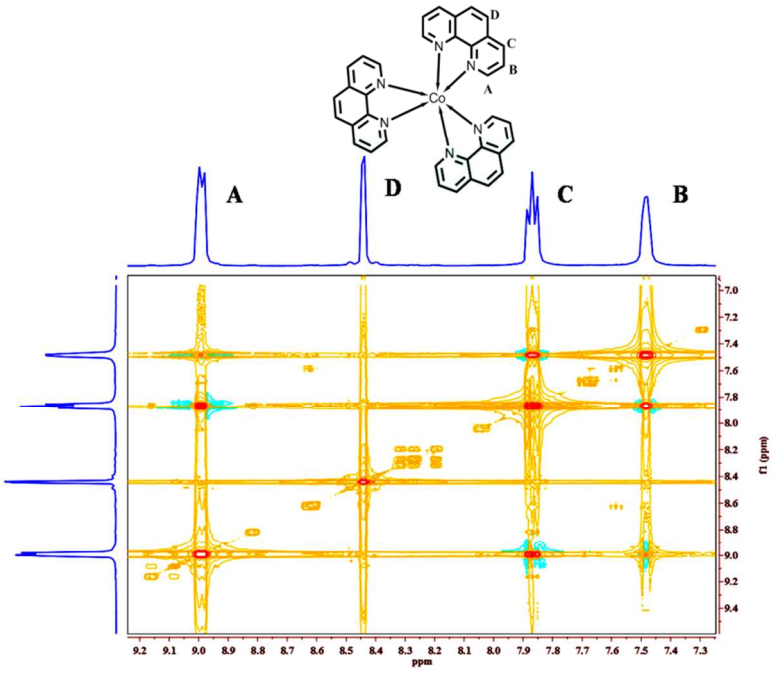


Figure S4. COSY of $[Co(phen)_3](PF_6)_3$.

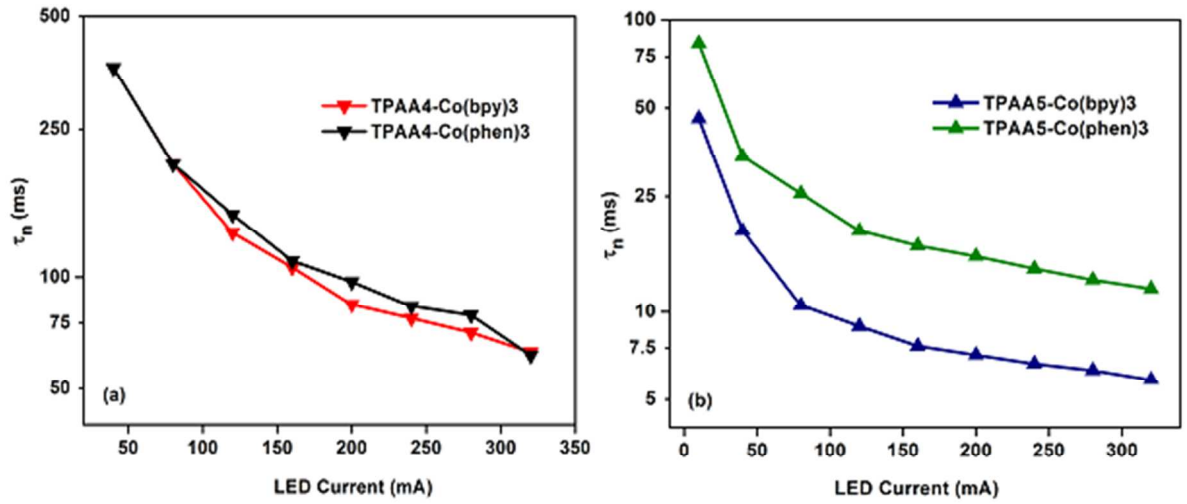


Figure S5. Electron Lifetime as a function of LED current measured by IMVS technique for devices fabricated using (a) TPAA4 employing $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$ (b) TPAA5 employing $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$.

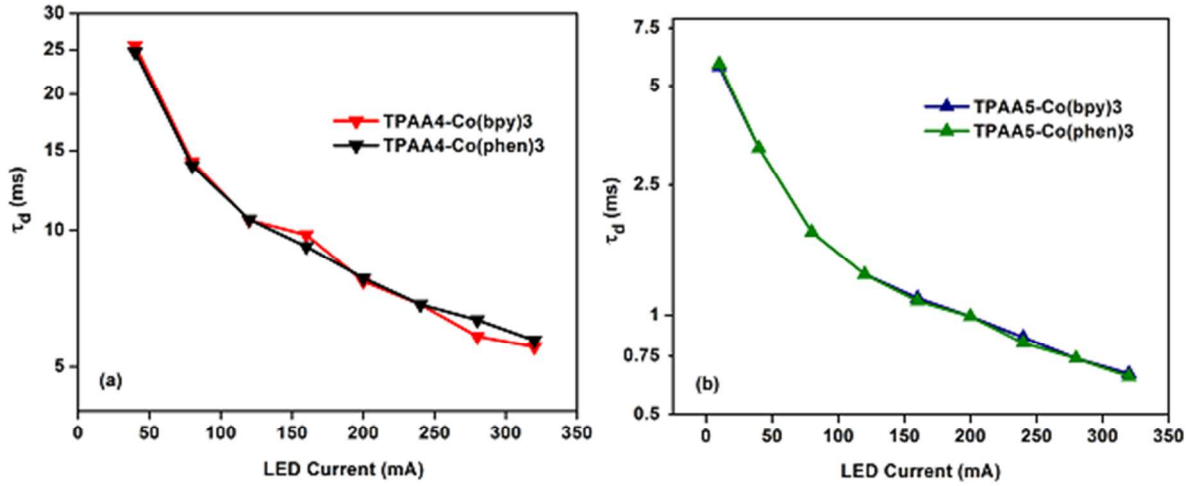


Figure S6. Transport time as a function of LED current measured by IMPS technique for devices fabricated using (a) TPAA4 employing $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$ (b) TPAA5 employing $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$.

REFERENCES

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