

Electronic supplementary information

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1. The specific synthesis and purification method of cobalt complexes

All of the complexes depicted in Figure 1 were synthesized and purification using the similar procedure^[1, 2].

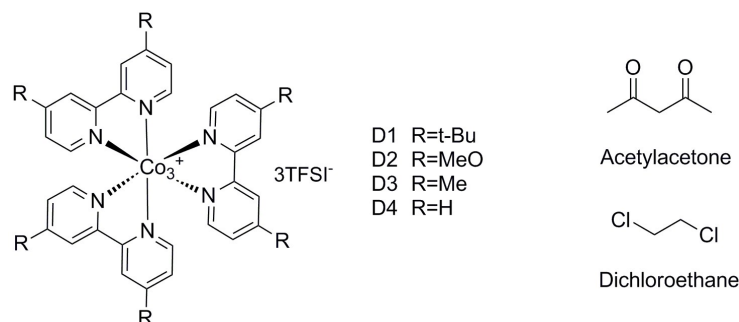


Fig.1 structure of co complexes and solvent

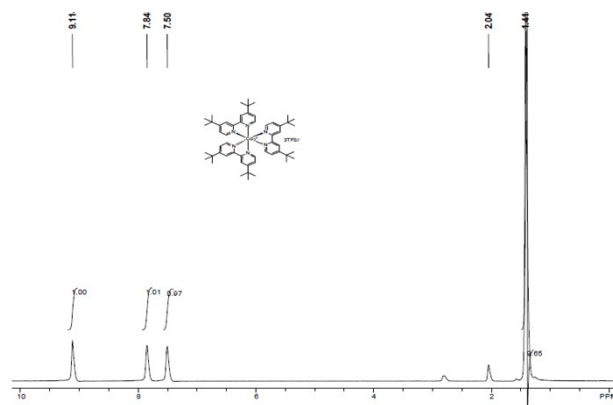
In short, 3 molar equivalents of ligand 268 mg was dissolved in methanol and water mixture solvent (V:V=1:2) 10.5ml with magnetic stirring and heated to 60 °C, the color of the solution was pale orange. The amount of methanol and water was adjusted according to the ligand solubility and the scale of the reaction so that the ligands were totally dissolved. 10mins later, 1.1 molar equivalent of cobalt (II) chloride hexahydrate 87.3mg was added, stirred for 30 minutes (D1 complexes were stirred for 60mins). After the mixture cooled to room temperature, 0.6ml H₂O₂ was added in order to oxidize the divalent cobalt, the color of the solution became dark. After 5 minutes intervals, the color of the solution changed from dark brown to light orange once 0.6ml HCl was added, (another 7ml methanol was added when prepared D1) and the mixture was heated to 75 °C for 2 hours. After the solution was cooled down to room temperature, followed by a concentrated solution lithium bis(trifluoromethanesulfonyl)imide 70% water solution (5 molar equivalents) was added slowly in the beginning to precipitate the crude product, stirred for 1 hour, filtered precipitates and dried at 60 °C.

The resulting compound was re-dissolved in methanol at 60 °C (D1 and D2 were dissolved in acetone), the amount of methanol (or acetone) was adjusted according to the crude solubility to make sure it was totally dissolved. Then temperature was cooled down to 5°C, the crystallized solid was just the purified product (a solid that varied from light brown to yellow). The product was characterized by ¹H-NMR and element analysis.

2 Characterization of co-complexes, ¹H-NMR in deuterated acetone

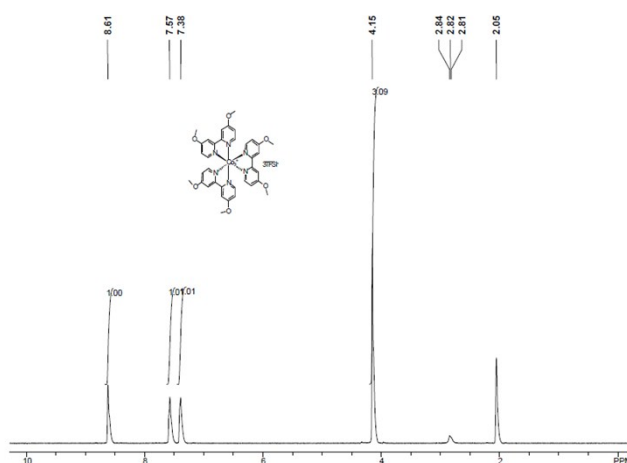
The testment was carried out by Bruker (DRX-400MHz) and Elementar (Vario EL cube).

2.1 D1, tris[(4,4'-di-tert-butyl-2,2'-bipyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)]



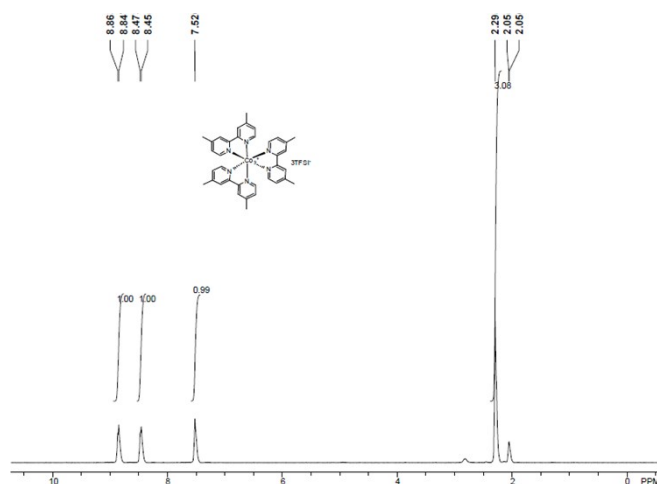
^1H NMR (400 MHz, Acetone- d_6) ppm: 9.11 (1H, s), 7.84(1H, s), 7.50 (1H,s), 1.41 (9H,s) .Element analysis: C 42.13%, N 7.28%, H 4.08%

2.2 D2, tris [(4, 4'-dimethoxy-2, 2'-bipyridine) cobalt (III) tris (bis (trifluoromethylsulfonyl) imide)]



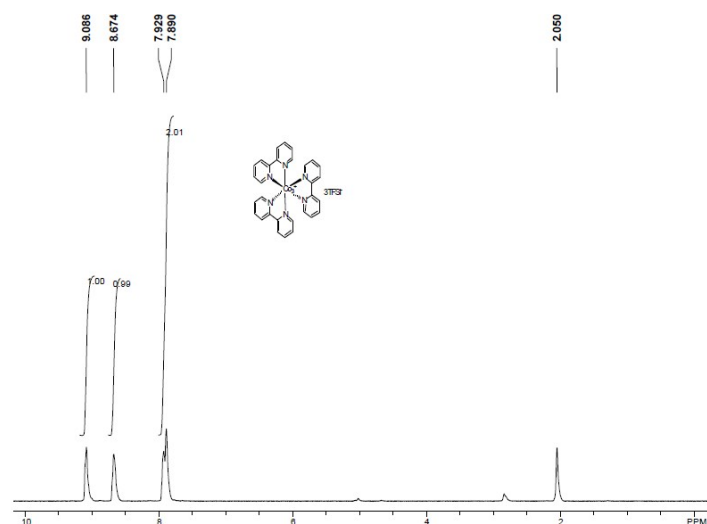
^1H NMR (400 MHz, Acetone- d_6) ppm: 8.61 (1H, s), 7.57(1H, s), 7.38 (1H,s), 4.15 (3H,s) .Element analysis: C 32.32%, N 7.98%, H 2.28%

2.3 D3, tris[(4,4'-dimethyl-2,2'-bipyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)]



^1H NMR (400 MHz, Acetone- d_6) ppm: 8.86-8.84 (1H, d), 8.47-8.45(1H, d), 7.52 (1H,s), 2.29 (3H,s) .Element analysis: C 34.58%, N 8.39%, H 2.27%

2.4 D4, tris[(2,2'-bipyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)]



^1H NMR (400 MHz, Acetone- d_6) ppm: 9.08 (1H, s), 8.67 (1H, s), 7.92-7.89 (2H, m). Element analysis: C 31.42%, N 9.08%, H 1.66%.

3 The date of the conductance of spiro-OMeTAD films and statistic relevance

Table 1 conductance of spiro-OMeTAD films and statistic relevance

dopants	conductance of spiro-OMeTAD films						Average	Standard Deviation
pristine spiro	0.00000225	0.00000432	0.00000331	0.00000287	0.00000295	0.00000198	2.94667E-06	8.29908E-7
without dopant	0.000204	0.000191	0.000248	0.000231	0.000209	0.0001838	2.11133E-4	2.22176E-5
t-Bu Co	0.000823	0.000761	0.000906	0.000847	0.000809	0.000882	0.000838	5.22226E-5
Me Co	0.00051	0.00059	0.00048	0.00041	0.0006	0.00055	0.000523333	7.20185E-5
MeO Co	0.000618	0.000575	0.000703	0.000668	0.000637	0.000626	0.000637833	4.39063E-5
Dinoyl Co	0.000432	0.000513	0.000381	0.000413	0.000487	0.000409	0.000439167	5.05348E-5

4 Devices performance with D1 complexes and FK209

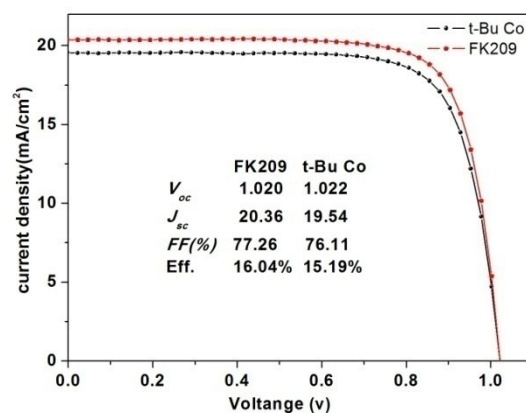


Fig.2 J-V characteristics for device fabricated using dopant D1 and FK209

Reference:

1. Burschka, J, F Kessler, M K Nazeeruddin, and M Grätzel, *Co (III) Complexes as p-Dopants in Solid-State Dye-Sensitized Solar Cells*. Chemistry of Materials, 2013. **25**(15): p. 2986-2990.
2. Noh, J H, N J Jeon, Y C Choi, M K Nazeeruddin, et al., *Nanostructured TiO₂/CH₃NH₃PbI₃ heterojunction solar cells employing spiro-OMeTAD/Co-complex as hole-transporting material*. Journal of Materials Chemistry A, 2013. **1**(38): p. 11842-11847.