Electronic Supplementary Material (ESI) for RSC Advances
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Supporting Information

A fluorine substituted phenanthroline-based ruthenium complex for dye-sensitized solar cells: the fluoro-substitution effect on the ancillary ligand

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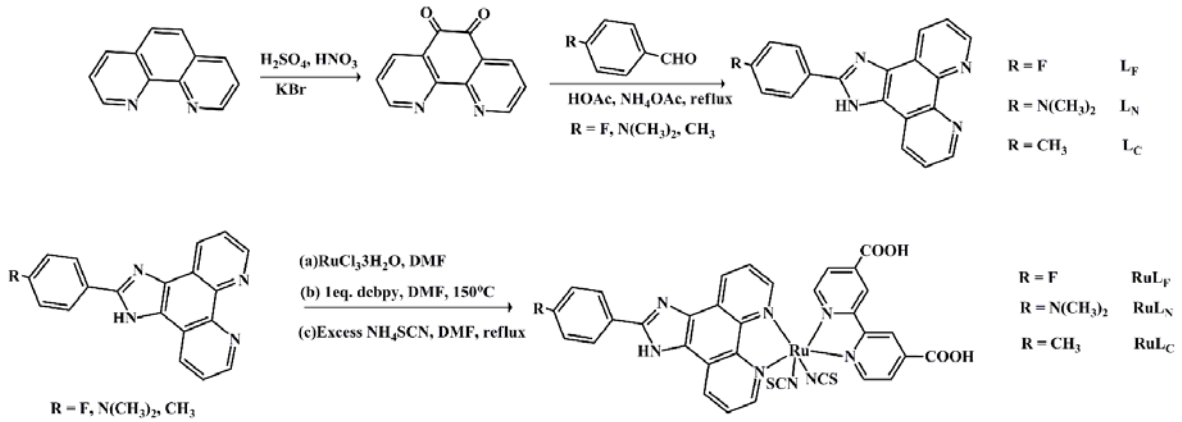
Experimental Section

Synthesis of 1,10-phenanthroline-5,6-dione. Solid KBr (12.0 g, 100 mmol,) and 1,10-phenanthroline (1.08 g, 10 mmol) were placed in a two-necked flask immersed in a ice/water bath, and then concentrated H_2SO_4 (98%, 20 mL) and concentrated HNO_3 (68%, 20 mL) as added dropwise with stirring. The resulting mixture was stirred for 30 min at room temperature and then for 4 h at 80 °C. The reaction was neutralized to pH=6 with aqueous ammonia solution after cooling to room temperature. CH_2Cl_2 was layered over the suspension and the two-phase mixture was stirred until the solid had dissolved. The organic phase was separated, washed with water and concentrated to dryness. The crude product was purified by recrystallization from CH_2Cl_2 and ethanol. Yield: 80%.

Synthesis of 2-(4-fluorinphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline ($\mathbf{L_F}$). A mixture of 1,10-phenanthroline-5,6-dione (210 mg, 1 mmol), ammonium acetate (1.54 g, 20 mmol), 4-fluorobenzaldehyde (136 mg, 1.1 mmol) and glacial acetic acid (30 mL) was heated at 120 °C for 4 h. After the reaction cooled to room temperature and neutralized with concentrated aqueous ammonia, the yellow precipitate was collected and washed with water. The crude product was purified by recrystallization from chloroform/ethanol to obtain 2-(4-fluorinphenyl)-1Himidaz[4,5-f][1,10] phenanthroline as a yellow-white solid. Yield: 70%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 7.45 (t, J = 8.7 Hz, 2H; phenyl), 7.81 (m, 2H, phenyl), 8.31(d, J = 2.7 Hz, 2H, phenyl), 8.87(m, 2H, phen), 9.01 (d, J = 3.9 Hz, 2H, phenyl). MS(ESI *m/z*): 315.10 ($[M+H]^+$), found 315.17 ($[M+H]^+$).

Synthesis of 4-(1H-imidazo[4,5-f]-[1,10]phenanthrolin-2-yl)-N,N-dimethylaniline ($\mathbf{L_N}$). $\mathbf{L_N}$ was synthesized by a procedure to $\mathbf{L_F}$ except that 4-(dimethylamino) benzaldehyde was used in place of 4-fluorobenzaldehyde. Yield: 65%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 3.01(s, 3H), 3.32(s, 3H), 6.87(d, J = 9.0 Hz, 2H, phenyl), 7.78(m, J = 6.9 Hz, 2H, phenyl), 8.88(d, J = 1.2 Hz, 2H, phenyl), 8.97(d, J = 3.0 Hz, 2H, phenyl). MS (ESI *m/z*): 311.13 ($[M+H]^+$), found 311.20 ($[M+H]^+$).

Synthesis of 2-(4-methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline ($\mathbf{L_C}$). $\mathbf{L_C}$ was synthesized by a procedure to $\mathbf{L_F}$ except that 4-methylbenzaldehyde was used in place of 4-fluorobenzaldehyde. Yield: 70%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 2.40 (s, 3H), 7.38(d, J = 8.1 Hz, 2H), 7.85(d, J = 4.2 Hz, 2H, phenyl), 8.15 (d, J = 7.8 Hz, 2H, phenyl), 8.90 (d, J = 4.5 Hz, 2H, phenyl), 8.99 (m, 2H; phenyl). MS (ESI *m/z*): 340.16 ($[M+H]^+$), found 340.23 ($[M+H]^+$).


H2SO4, HNO3
KBr
R
CHO
HOAc, NH4OAc, reflux
R = F, N(CH3)2, CH3
R = F
R = N(CH3)2
R = CH3
LF
LN
LC
(a)RuCl3 3H2O, DMF
(b) 1eq. dcbpy, DMF, 150°C
(c)Excess NH4SCN, DMF, reflux
R = F, N(CH3)2, CH3
COOH
Ru
SCN
NCS
RuLF
RuLN
RuLC

Scheme S1

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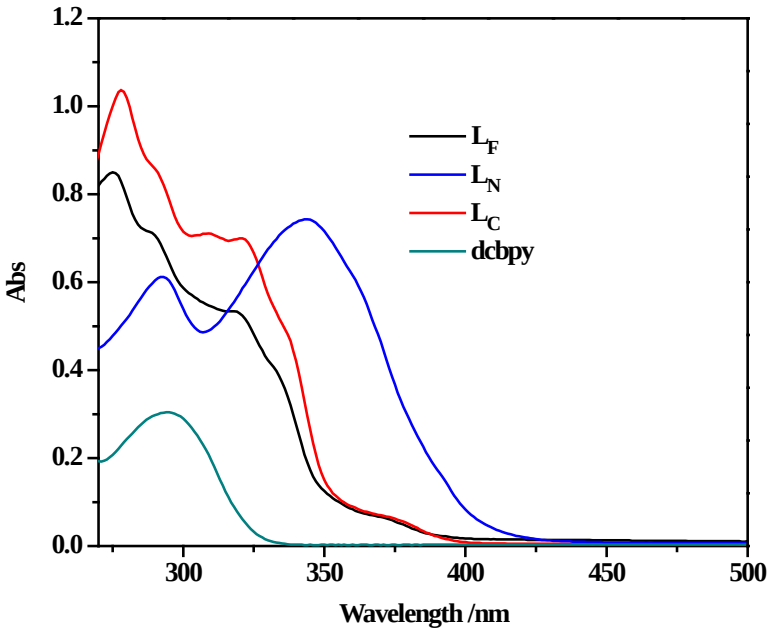

Fig. S1 Absorption spectra of $\mathbf{L_F}$, $\mathbf{L_N}$, $\mathbf{L_C}$, and H_2dcbpy in DMF

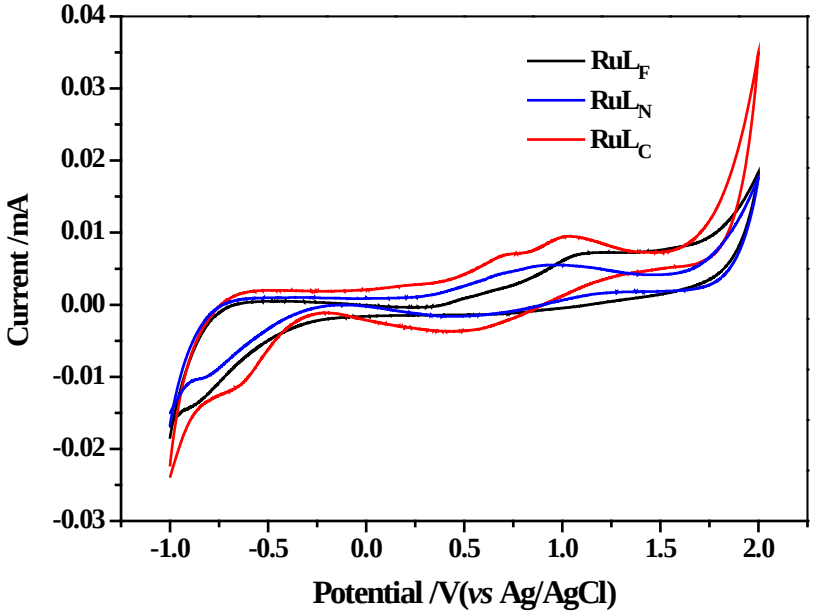

Fig. S2 Cyclic voltammograms of $\mathbf{RuL_F}$, $\mathbf{RuL_N}$, and $\mathbf{RuL_C}$ in a DMF solution of $TBAPF_6$ (0.1 M). (The concentrations of three dyes were 3×10^{-3} M).

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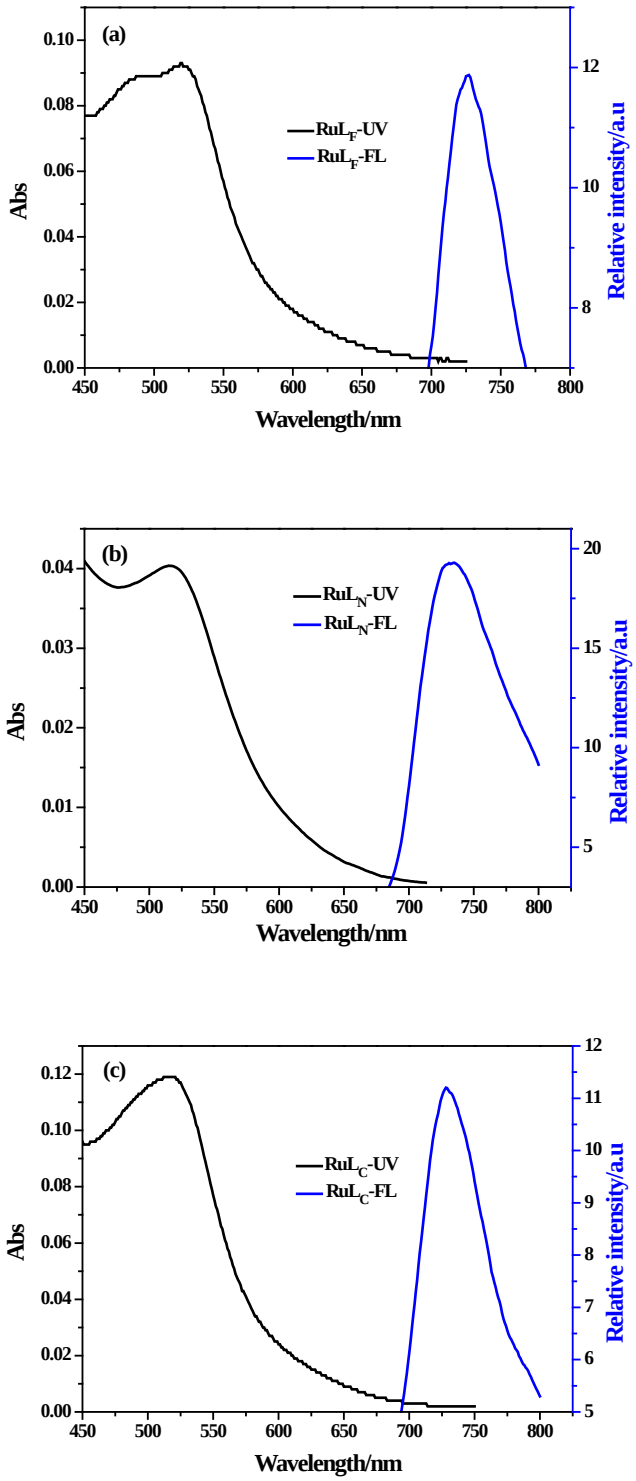

Fig. S3 Absorption and emission spectra of (a) **RuL$_F$**, (b) **RuL$_N$**, and (c) **RuL$_C$** measured in DMF.

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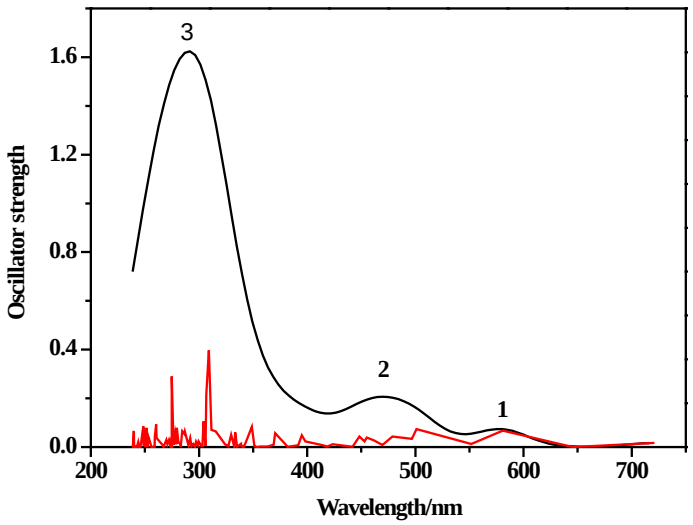

Fig. S4 computed spectrum of **RuL$_F$**

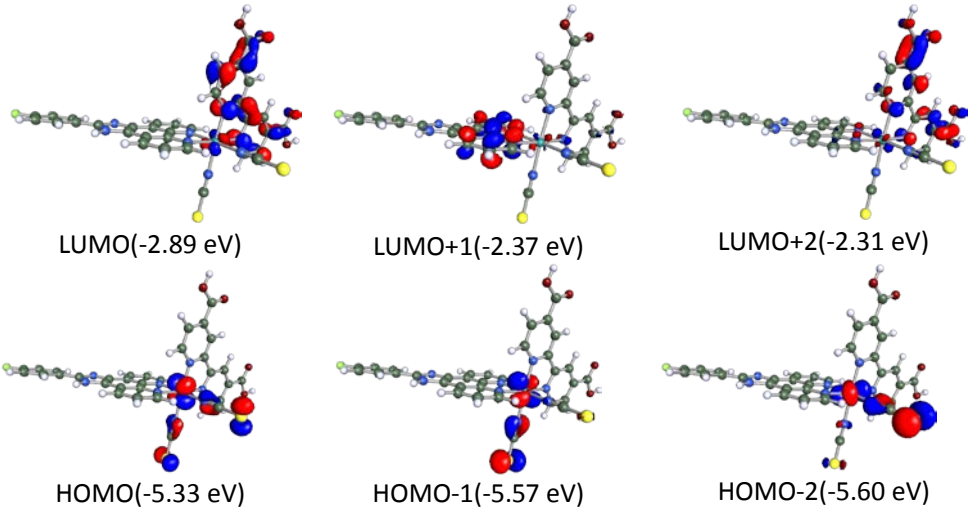

Fig. S5 Computed isosurface plots of selected molecular orbitals (from HOMO-2 to LUMO+2) of dye **RuL$_F$** , which are mainly involved in the optically active electronic transitions 1 and 2.

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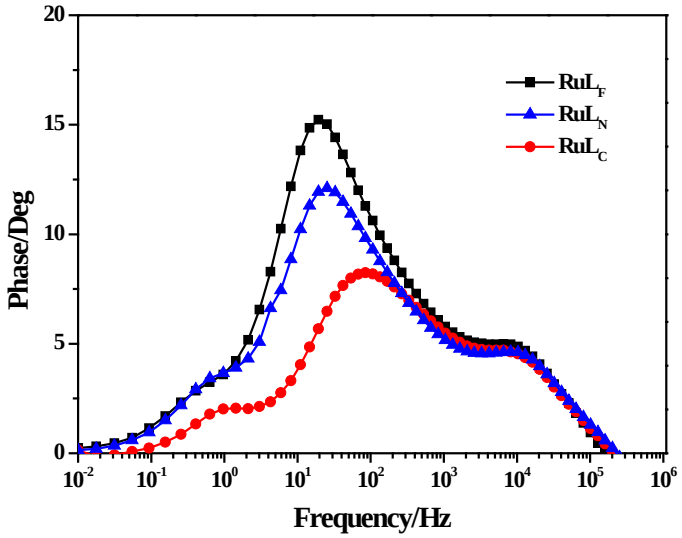

Fig. S6 EIS bode plots (i.e. the phase of the impedance *vs* the frequency) for DSSCs based on **RuL$_F$**, **RuL$_N$**, and **RuL$_C$** dyes.

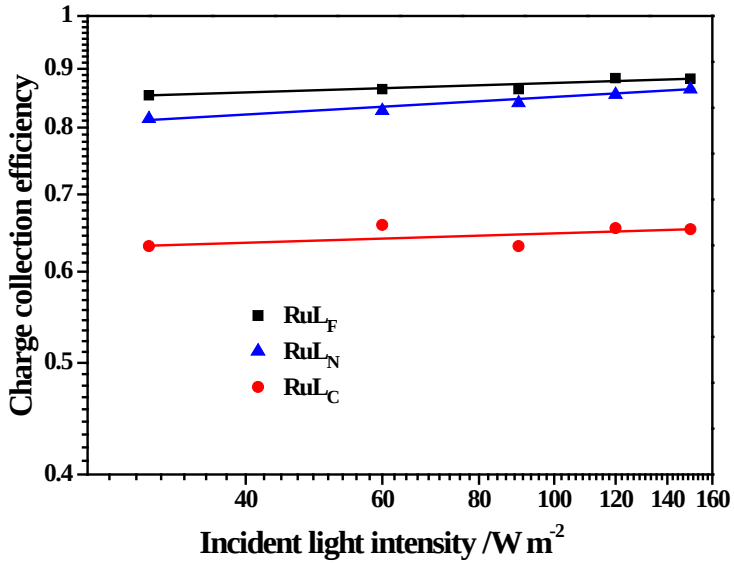

Fig. S7 Charge collection efficiencies from IMPS and IMVS for DSSCs based on **RuL$_F$**, **RuL$_N$**, and **RuL$_C$** dyes.

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Table S1 Character table of calculated vertical excitations 1, 2, and 3 for dye **RuL$_F$**[a]

Dye	Elec. transition	Calcn. (nm)	Exp. (nm)	Composition	
RuL$_F$	1	580	512	HOMO-2→LUMO	70.6%
				HOMO→LUMO+2	12.8%
	2	501	470	HOMO-1→LUMO+1	38.5%
				HOMO→LUMO+2	28.4%
	3	311	302	HOMO-6→LUMO+2	31.4%
				HOMO-8→LUMO	23.4%
				HOMO-4→LUMO+4	18.4%

[a] Contributions below 12% are not shown.

Table S2 Influence of CDCA on the photovoltaic performance parameters

dye	J_{sc}/mA cm^{-2}	V_{oc}/mV	*FF*	η (%)
RuL$_F$	14.02	675	0.72	6.85
RuL$_F$-CDCA	15.39	656	0.72	7.28