Supporting Information

Carbene-based Ruthenium Photosensitizers

Contents	Page
(1) Synthesis of CifPR sensitizer	S 1
(2) Theoretical calculation of the locations of the HOMOs and LUMOs	S 2
(3) Crystal structure of compound 4	. S3
(4) ¹ H and ¹³ C NMR spectra of CiPoR, CifPoR and CifPR sensitizers	S5

1. Synthesis of CifPR sensitizer



11: Compound **10** (200 mg, 1.80 mmol) and imidazole (147 mg, 2.16 mmol) in a round-bottom flask were dissolved in DMF (9 mL) at 0 °C. Sodium hydride (60% dispersion in mineral oil, 95 mg, 2.38 mmol) was added and stirred at room temperature for 10 min. The mixture was then warmed to 80 °C and stirred overnight. The resulting solution was cooled to room temperature and the solvent was evaporated under reduced pressure. After adding CH_2Cl_2 (50 mL), the organic phase was extracted with H_2O (3 × 25 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The dried residue was dissolved in DMF (8 mL) and 3,5-difluorobenzyl bromide (410 mg, 1.98 mmol) was added to the solution, which was then stirred at 100 °C for 12 h. After the removal of solvent, the crude compound **11** (560 mg, 85%) was washed with ether (15 mL) and used in the subsequent step without

further purification. ¹H NMR (300 MHz, CDCl₃): δ 2.54 (s, 3H), 6.82 (tt, J = 2.4, 8.7 Hz, 1H), 7.20-7.27 (m, 3H), 7.54 (s, 1H), 8.24-8.25 (m, 2H), 8.35 (d, J = 4.8 Hz, 1H), 11.80 (s, 1H).

4: Prepared from compound **11** using a method similar to that described for the synthesis of easter **8.** ¹H NMR (300 MHz, d_6 -DMSO): δ 2.38 (s, 3H), 3.90 (s, 3H), 4.06 (s, 3H), 5.67 (d, J = 14.7 Hz, 1H), 5.90 (d, J = 14.7 Hz, 1H), 6.87 (d, J = 4.8 Hz, 1H), 7.16-7.23 (m, 2H), 7.29-7.31 (m, 2H), 7.44 (dd, J =1.8, 6.0 Hz, 1H), 7.95-8.01 (m, 3H), 8.45 (dd, J = 1.8, 6.0 Hz, 1H), 8.58 (d, J = 2.4 Hz, 1H), 8.97 (s, 1H), 9.23 (s, 1H), 9.47 (d, J = 5.7 Hz); $C_{32}H_{25}F_2N_7O_4S_2Ru$ (M) 775.0421, found 775.0427.

Dye 3 : Prepared from compound **4** using a method similar to that described for the synthesis of dye **1**. Yield: 95%;¹H NMR (500 MHz, d_6 -DMSO): δ 2.38 (s, 3H), 5.68 (d, J = 14.5 Hz, 1H), 5.90 (d, J = 14.5 Hz, 1H), 6.87 (d, J = 6.0 Hz, 1H), 7.19 (t, J = 9.5 Hz, 1H), 7.24 (d, J = 6.0 Hz, 1H), 7.30 (d, J = 6.0 Hz, 1H), 7.41 (d, J = 1.5, 6.0 Hz, 1H), 7.91 (d, J = 6.0 Hz, 1H), 7.94 (d, J = 2.5 Hz, 1H), 8.00 (s, 1H), 8.44 (d, J = 5.5 Hz, 1H), 8.57 (d, J = 2.5 Hz, 1H), 8.87 (s, 1H), 9.12 (s, 1H), 9.43 (d, J = 5.5 Hz, 1H); ¹³C NMR (125 MHz, d_6 -DMSO add KOH): δ 20.7, 51.2, 103.4 (t, $J_{CF} = 26.3$ Hz), 111.4, 111.8 (dd, $J_{CF} = 6.3$, 20.0 Hz), 117.5, 121.8, 121.9, 122.7, 124.0, 124.8, 126.1, 133.4, 134.5, 141.6 (t, $J_{CF} = 8.8$ Hz), 148.0, 149.6, 149.7, 149.9, 150.0, 154.6, 155.0, 155.1, 157.8, 162.4 (dd, $J_{CF} = 12.5, 245.0$ Hz), 165.0, 165.5, 198.5; C₃₀H₂₁F₂N₇O₄S₂Ru (M) 747.0108, found 747.0102.

2. Theoretical calculation for the location of HOMOs and LUMOs

Geometry optimization and the location of the frontier orbitals of CifPR were computed using the Hyperchem 7.5 program and the ZINDO/1 parameter set. The structure of the complex was optimized without symmetry or conformational constraints.



Figure S2. Frontier orbital representations of the sensitizer CifPR.

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3. Crystal structure of compound 4



Figure S1. Crystal structure of 4

Crystal data for C₃₂H₂₅F₂N₇O₄RuS₂[**4**]: 0.25 × 0.02 × 0.02 mm³; M = 774.78; monoclinic; space group C1 c1; a = 15.827(2) Å; b = 17.404(3) Å; c = 15.344(2) Å; $\alpha = 90^{\circ}$; $\beta = 109.473(3)^{\circ}$; $\gamma = 90^{\circ}$; V = 3984.7(10) Å³; Z = 4; $\rho_{calcd} = 1.292$ Mg/m³; $\mu = 0.548$ mm⁻¹; F(000) = 1568; T = 100(2) K; data collection: $1.80 \leq \theta \leq 26.46^{\circ}$; reflections collected: 26,959; independent reflections: 7550 [R(int) = 0.0651]; refinement method: full-matrix least-squares on F^2 ; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0402$; $wR_2 = 0.0820$; R indices (all data): $R_1 = 0.0535$; $wR_2 = 0.0861$. **CCDC 789379** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

	Table 51. Selected l	John distances for e	stel 4
Bond	Bond length [Å]	Bond	Bond length [Å]
Ru(1)-C(8)	2.004(5)	C(11)-H(11A)	0.9900
Ru(1)-N(1)	2.039(5)	C(11)-H(11B)	0.9900
Ru(1)-N(6)	2.051(5)	C(12)-C(13)	1.378(6)
Ru(1)-N(2)	2.053(5)	C(12)-C(17)	1.381(7)
Ru(1)-N(3)	2.068(5)	C(13)-C(14)	1.382(8)
Ru(1)-N(7)	2.111(4)	C(13)-H(13)	0.9500
S(1)-C(1)	1.633(6)	C(14)-F(1)	1.356(7)

Table S1.	Selected	bond	distances	for	ester	4
	Deletted	oonu	unstances	101	Cotor	-

S(2)-C(2)	1.665(6)	C(14)-C(15)	1.364(8)
N(1)-C(1)	1.177(6)	C(15)-C(16)	1.364(7)
N(2)-C(2)	1.127(6)	C(15)-H(15)	0.9500
N(3)-C(7)	1.346(7)	C(16)-F(2)	1.356(7)
N(3)-C(3)	1.355(6)	C(16)-C(17)	1.363(7)
N(4)-C(9)	1.387(6)	C(17)-H(17)	0.9500
N(4)-C(8)	1.391(7)	C(18)-H(18A)	0.9800
N(4)-C(7)	1.396(6)	C(18)-H(18B)	0.9800
N(5)-C(8)	1.348(6)	C(18)-H(18C)	0.9800
N(5)-C(10)	1.423(6)	C(19)-C(20)	1.393(7)
N(5)-C(11)	1.457(5)	C(19)-H(19)	0.9500
N(6)-C(19)	1.328(6)	C(20)-C(21)	1.390(6)
N(6)-C(23)	1.387(6)	C(20)-H(20)	0.9500
N(7)-C(28)	1.331(6)	C(21)-C(22)	1.376(6)
N(7)-C(24)	1.361(6)	C(21)-C(29)	1.504(6)
O(1)-C(29)	1.204(5)	C(22)-C(23)	1.386(6)
O(2)-C(29)	1.327(5)	C(22)-H(22)	0.9500
O(2)-C(30)	1.451(5)	C(23)-C(24)	1.462(6)
O(3)-C(31)	1.193(5)	C(24)-C(25)	1.391(7)
O(4)-C(31)	1.336(5)	C(25)-C(26)	1.405(6)
O(4)-C(32)	1.439(5)	C(25)-H(25)	0.9500
C(3)-C(4)	1.401(8)	C(26)-C(27)	1.383(6)
C(3)-H(3)	0.9500	C(26)-C(31)	1.504(6)
C(4)-C(5)	1.369(9)	C(27)-C(28)	1.392(6)
C(4)-H(4)	0.9500	C(27)-H(27)	0.9500
C(5)-C(6)	1.379(8)	C(28)-H(28)	0.9500
C(5)-C(18)	1.507(8)	C(30)-H(30A)	0.9800
C(6)-C(7)	1.388(7)	C(30)-H(30B)	0.9800
C(6)-H(6)	0.9500	C(30)-H(30C)	0.9800
C(9)-C(10)	1.321(7)	C(32)-H(32A)	0.9800
C(9)-H(9)	0.9500	C(32)-H(32B)	0.9800
C(10)-H(10)	0.9500	C(32)-H(32C)	0.9800
C(11)-C(12)	1.506(6)		

4. ¹H and ¹³C NMR spectra of CiPoR, CifPoR and CifPR sensitizers





