Donor-substituted Phenyl-π-chromones: Electrochemiluminescence and Intriguing Electronic Properties

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Electronic Supplementary Information

Characterization Data for compounds**,** UV and fluorescence spectra, and CV curves for **1-5** are furnished below. A comparative ECL and PL spectra and the X-ray crystallographic data of **4** are also appended at the end.

3-Phenylethynyl-chromen-4-one (1): m.p.: 150 – 153 °C ^{1}H-NMR (δ, ppm): 8.26 (d, *J* = 8 Hz, 1H), 8.22 (s, 1H), 7.67 (t, *J* = 8 Hz, 1H), 7.55 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 8 Hz, 1H), 7.32 (m, 3H); ^{13}C NMR (δ): (100 MHz,$CDCl_3$): δ 79.43, 94.95, 111.28, 118.09, 112.49, 123.41, 125.62, 126.11, 128.14, 128.50, 131.66, 133.85, 155.72, 157.69, 175.12; Mass Spectra (*m/z*): 246.0682 (M^+).

3-*p*-Tolylethynyl-chromen-4-one (**2**): m.p.: 136 – 138 °C; ^{1}H NMR (δ, ppm): 8.26 (d, *J* = 8 Hz, 1H), 8.20 (s, 1H), 7.67 (t, *J* = 8 Hz, 1H), 7.43 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (δ): (100 MHz, $CDCl_3$, δ, ppm): 21.66, 78.75, 95.18, 111.45, 118.07, 119.43, 123.42, 125.56, 126.11, 128.91, 131.56, 133.78, 138.66, 155.72, 157.52, 175.17; Mass Spectra (*m/z*): 260.0839 (M^+).

3-(4-Methoxy-phenylethynyl)-chromen-4-one (3): m.p.: 130 – 131 °C; ^{1}H NMR (δ, ppm): 8.25, (d, *J* = 8 Hz, 1H), 8.19 (s, 1H), 7.66 (t, *J* = 8.8 Hz, 1H), 7.45 (m, 4H), 6.85 (d, *J* = 8 Hz, 2H), 3.8 (s, 3H); ^{13}C NMR (δ): (100 MHz, $CDCl_3$): 55.27, 78.06, 94.97, 111.46, 113.77, 114.56, 118.03, 123.32, 125.48, 126.01, 133.11, 133.72, 155.65, 157.33, 159.59, 175.18; Mass Spectra(*m/z*): 276.0787 (M^+).

3-(4-Isopropoxy-phenylethynyl)-chromen-4-one (4): m.p.: 130 – 133 °C; ^{1}H NMR (δ, ppm): 8.25, (d, *J* = 8 Hz, 1H), 8.18 (s, 1H), 7.66 (t, *J* = 8 Hz, 1H), 7.43 (m, 4H), 6.82 (d, *J* = 6.8 Hz, 2H), 4.54 (t, *J* = 6.4 Hz, 1H), 1.32 (d, *J* = 6 Hz, 6H); ^{13}C NMR (δ): (100 MHz, $CDCl_3$): 22.41, 70.23, 78.26, 95.48, 111.93, 114.56, 115.80, 118.39, 123.74, 125.84, 126.44, 133.52, 134.06, 156.06, 157.63, 158.39, 175.55; Mass Spectra (*m/z*): 304.1098 (M^+).

3-[4-(2-Ethyl-hexyloxy)-phenylethynyl]-chromen-4-one (5): viscous liquid; ^{1}H NMR (δ, ppm):8.25, (d, *J* = 8 Hz, 1H), 8.18 (s, 1H), 7.66 (t, *J* = 8.8 Hz, 1H), 7.43 (m, 4H), 6.84 (d, J = 6.8 Hz, 2H), 3.83 (d, *J* = 6 Hz, 2H), 1.9 (m, 2H), 1.4 (m, 7H), 0.90 (m, 6H); ^{13}C NMR (δ): (100 MHz, $CDCl_3$): 11.21, 14.19, 23.11, 23.89, 29.13, 30.54, 39.34, 70.50, 76.68, 77.00, 77.32, 77.92, 95.19, 111.57, 114.23, 114.34, 118.04, 123.37, 125.48, 126.07, 133.09, 133.72, 155.69, 157.28, 159.49, 175.21; Mass Spectra (*m/z*): 374.1885 (M^+).

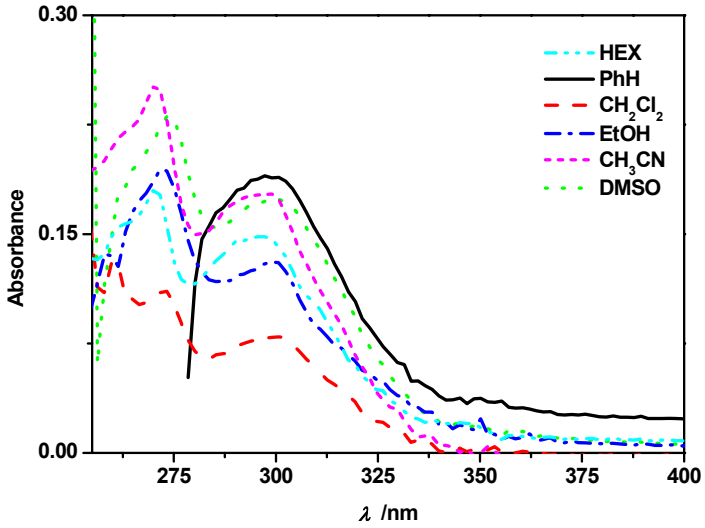

Figure S-1. UV-Spectra of **1** in various solvents.

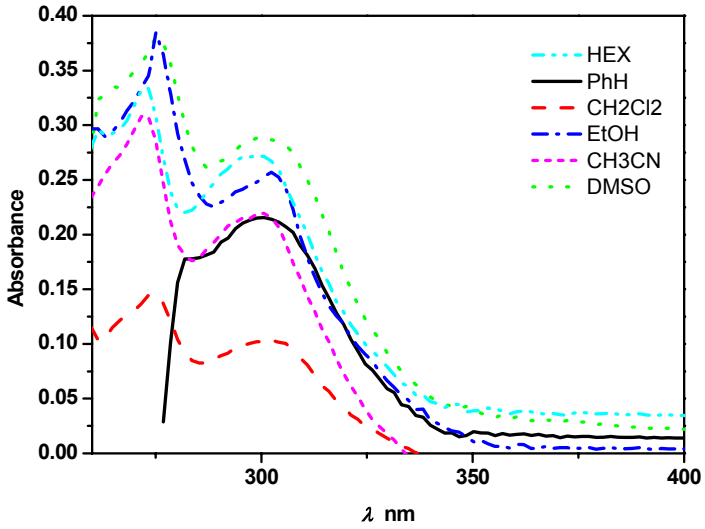

Figure S-2. UV Spectra of **2** in various solvents.

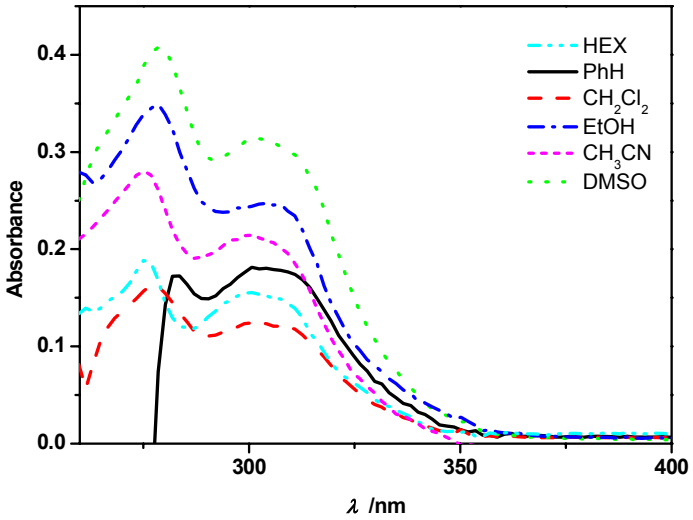

Figure S-3. UV Spectra of **3** in various solvents.

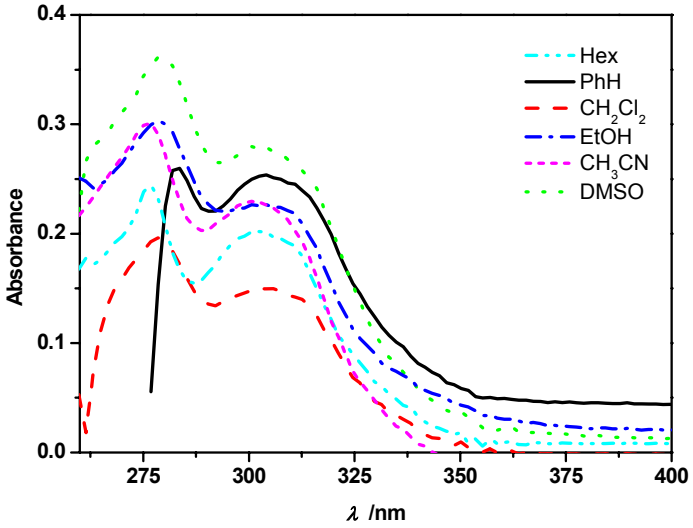

Figure S-4. UV Spectra of **4** in various solvents.

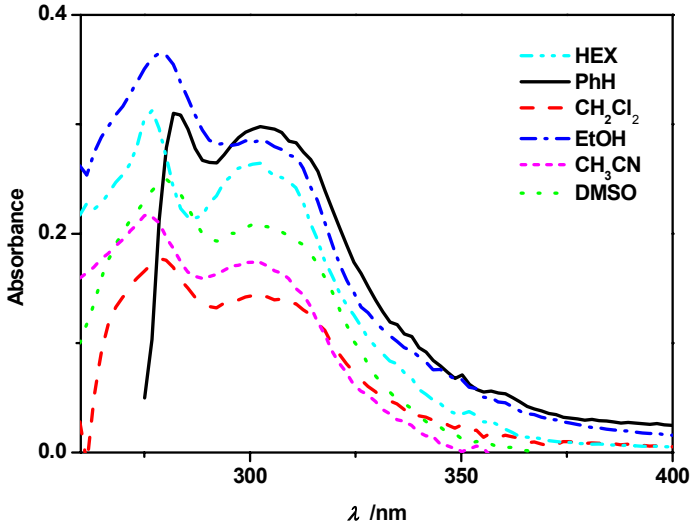

Figure S-5. UV Spectra of **5** in various solvents.

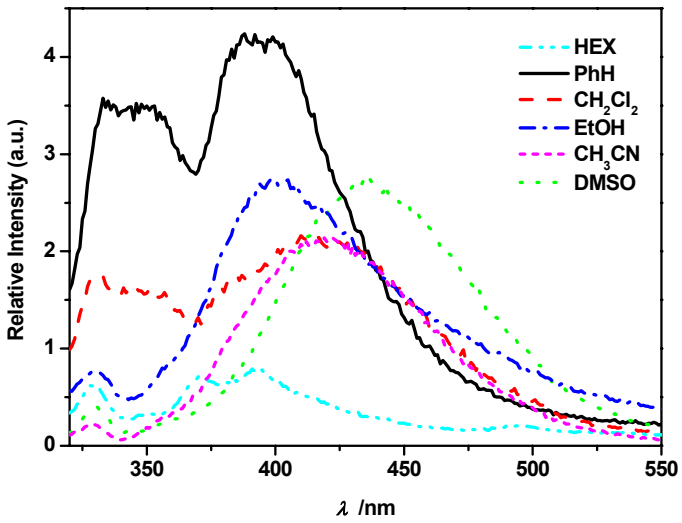

Figure S-6. Fluorescence spectra of **1** in various solvents.

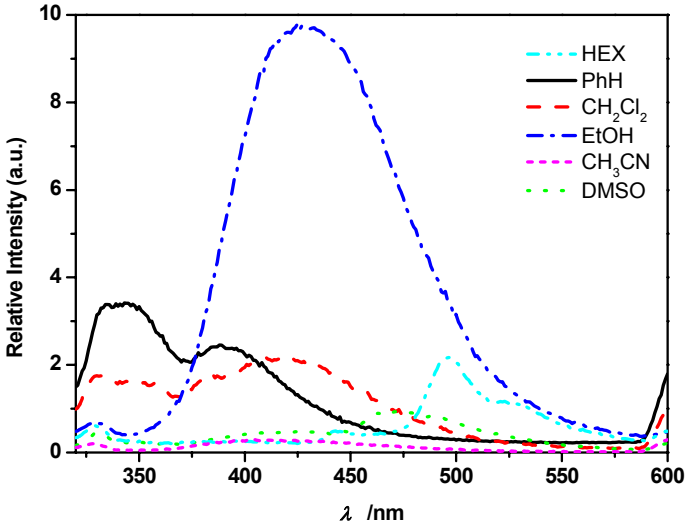

Figure S-7. Fluorescence spectra of **2** in various solvents.

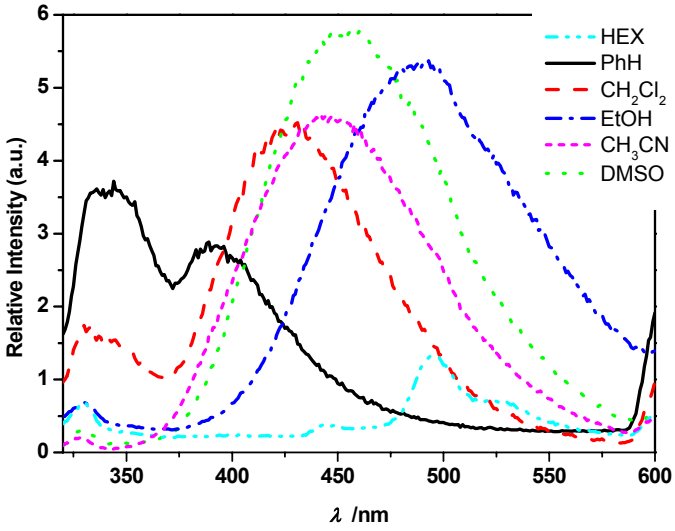

Figure S-8. Fluorescence spectra of **3** in various solvents.

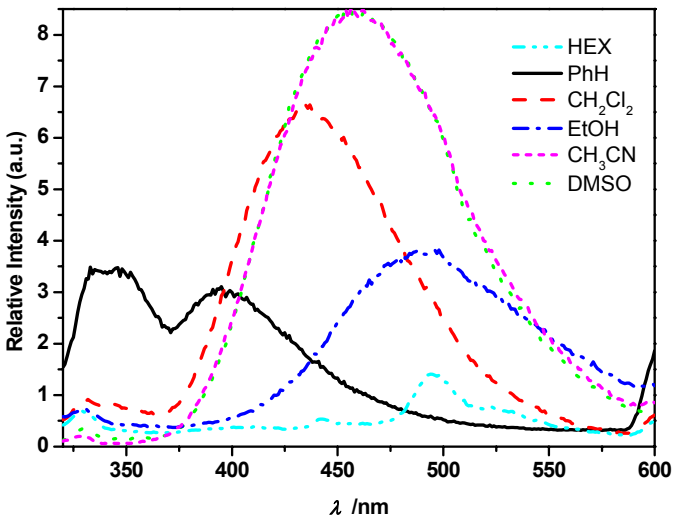

Figure S-9. Fluorescence spectra of **4** in various solvents.

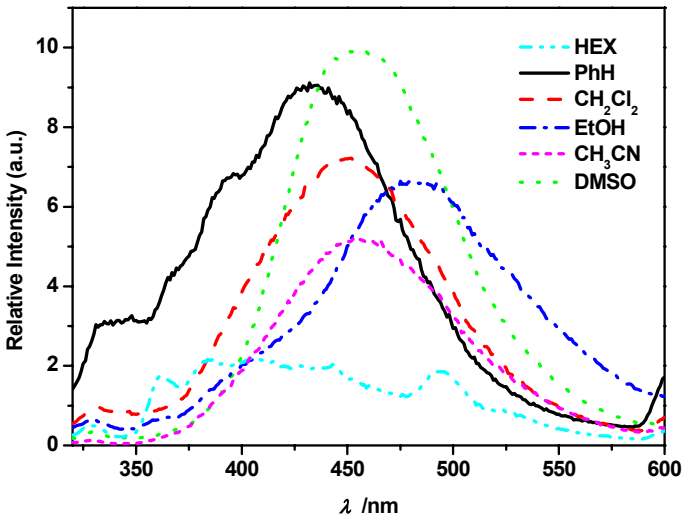

Figure S-10. Fluorescence Spectra of **5** in various solvents.

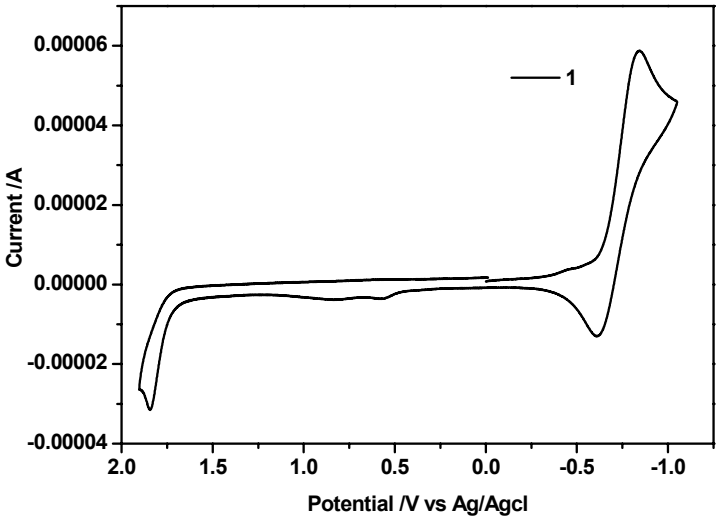

Figure S-11. Typical CV curve for compound **1** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP).

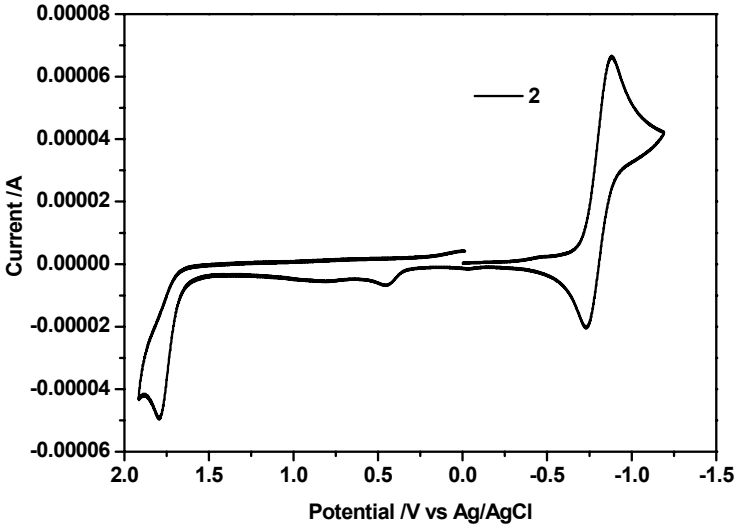

Figure S-12. Typical CV curve for compound **2** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP).

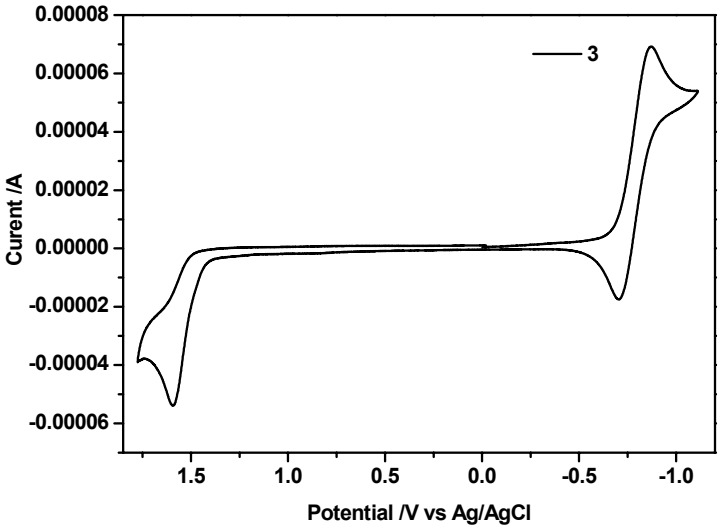

Figure S-13. Typical CV curve for compound **3** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP).

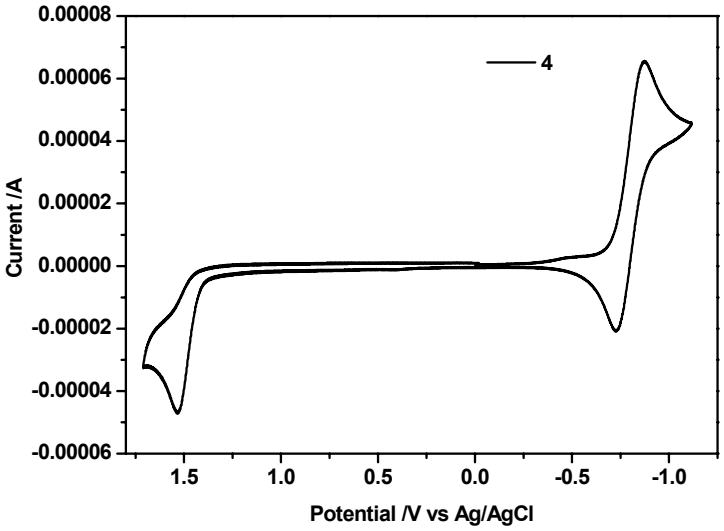

Figure S-14. Typical CV curve for compound **4** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP).

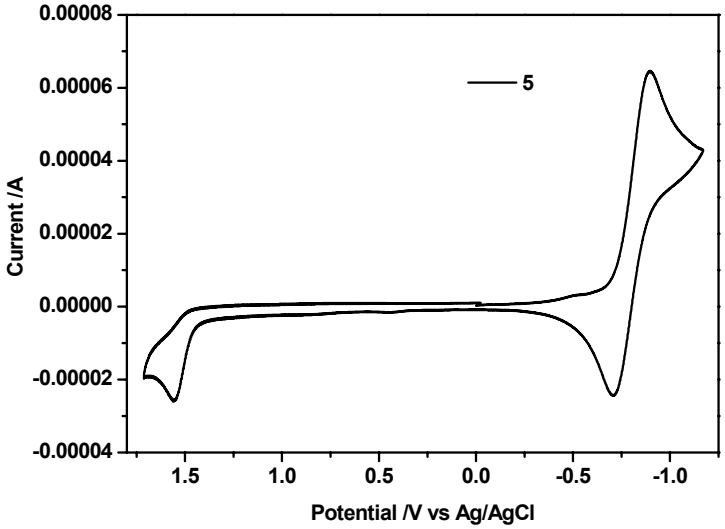

Figure S-15. Typical CV curve for compound **5** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP).

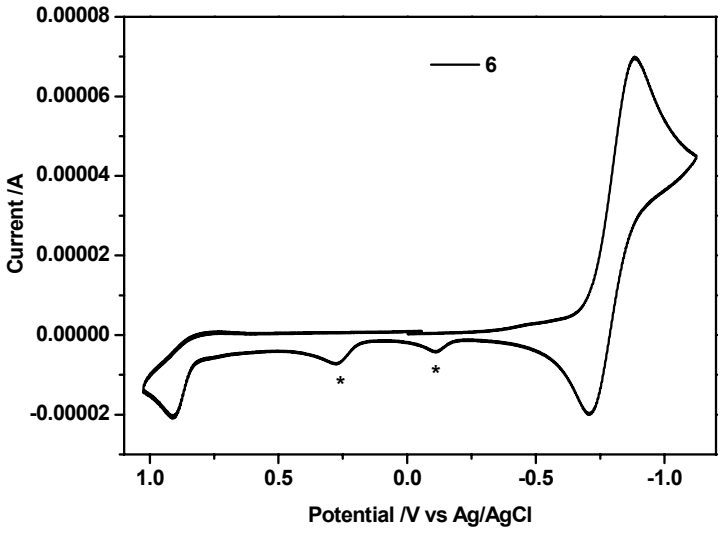

Figure S-16. Typical CV curve for compound **6** against Ag/AgCl recorded in ACN (10^{-3}M with 50 mM TBAP); * indicates interference caused by to incompletely removed oxygen/impurity.

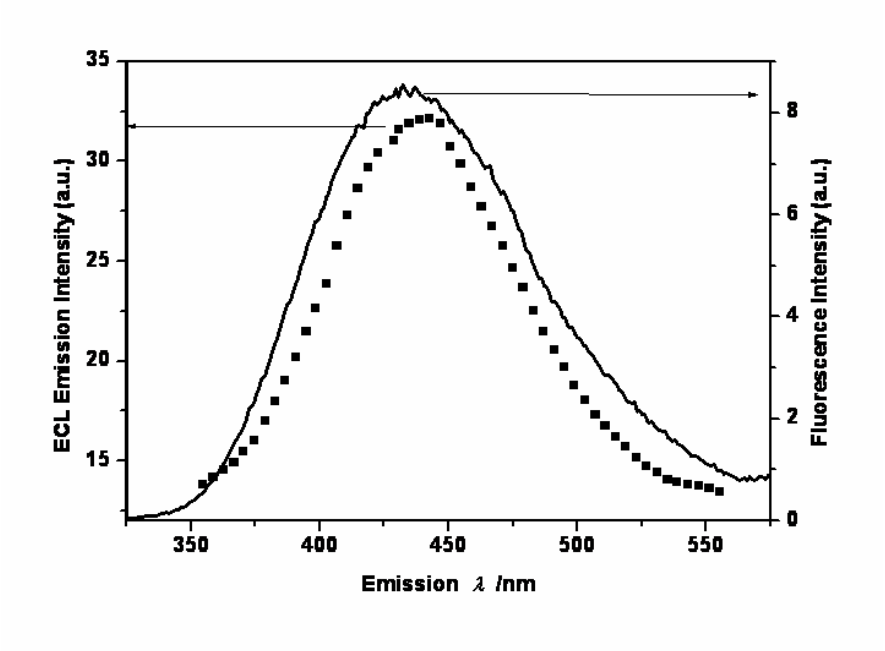

Figure S-17. Comparative ECL (Squares) and PL (solid line) spectra of compound **4** showing close overlap of both the spectra recorded in ACN at room temperature.

Table 1. Crystal data and structure refinement for IC10593 Compound 4.

Identification code	ic10593
Diffractometer used	Nonius KappaCCD
Empirical formula	$C_{20}H_{16}O_3$
Formula weight	304.33
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.2400(7) Å alpha = 90° b = 6.3210(4) Å beta = 98.915(3)° c = 36.476(2) Å gamma = 90°
Volume, Z	3243.6(3) $Å^3$, 8
Density (calculated)	1.246 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	1280
Crystal size	0.30 x 0.20 x 0.15 mm
θ range for data collection	1.13 to 24.97°
Limiting indices	$-15 \le h \le 15$, $-7 \le k \le 7$, $-32 \le l \le 42$
Reflections collected	10293
Independent reflections	5291 (R_{int} = 0.1081)
Absorption correction	Multi-scan
Max. and min. transmission	0.998 and 0.922
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5200 / 0 / 416
Goodness-of-fit on F^2	1.672
Final R indices [I>2σ(I)]	R1 = 0.1601, wR2 = 0.3582
R indices (all data)	R1 = 0.2998, wR2 = 0.3932
Extinction coefficient	0.035(5)
Largest diff. peak and hole	0.580 and -0.528 $eÅ^{-3}$

Table 2. Bond lengths [Å] and angles [°] for 10593. Compound **4**.

O(1)-C(1)	1.359(9)	O(1)-C(9)	1.390(10)
O(2)-C(3)	1.242(10)	O(3)-C(15)	1.362(9)
O(3)-C(18)	1.447(10)	O(4)-C(21)	1.363(10)
O(4)-C(29)	1.377(10)	O(5)-C(23)	1.244(11)
O(6)-C(35)	1.357(9)	O(6)-C(38)	1.439(11)
C(1)-C(2)	1.357(12)	C(2)-C(10)	1.417(12)
C(2)-C(3)	1.450(12)	C(3)-C(4)	1.439(11)
C(4)-C(9)	1.364(12)	C(4)-C(5)	1.435(12)
C(5)-C(6)	1.367(12)	C(6)-C(7)	1.40(2)
C(7)-C(8)	1.38(2)	C(8)-C(9)	1.395(11)
C(10)-C(11)	1.181(11)	C(11)-C(12)	1.437(12)
C(12)-C(13)	1.363(12)	C(12)-C(17)	1.386(12)
C(13)-C(14)	1.362(11)	C(14)-C(15)	1.366(12)
C(15)-C(16)	1.400(12)	C(16)-C(17)	1.378(10)
C(18)-C(19)	1.512(11)	C(18)-C(20)	1.541(13)
C(21)-C(22)	1.356(12)	C(22)-C(23)	1.413(12)
C(22)-C(30)	1.447(12)	C(23)-C(24)	1.466(11)
C(24)-C(25)	1.373(12)	C(24)-C(29)	1.375(12)
C(25)-C(26)	1.374(12)	C(26)-C(27)	1.354(14)
C(27)-C(28)	1.391(13)	C(28)-C(29)	1.375(11)
C(30)-C(31)	1.173(11)	C(31)-C(32)	1.448(11)
C(32)-C(33)	1.375(11)	C(32)-C(37)	1.409(12)
C(33)-C(34)	1.374(10)	C(34)-C(35)	1.372(12)
C(35)-C(36)	1.371(12)	C(36)-C(37)	1.396(11)
C(38)-C(40)	1.504(14)	C(38)-C(39)	1.506(12)

C(1)-O(1)-C(9)	118.6(7)	C(15)-O(3)-C(18)	122.0(7)
C(21)-O(4)-C(29)	118.7(7)	C(35)-O(6)-C(38)	119.6(8)
C(2)-C(1)-O(1)	125.8(8)	C(1)-C(2)-C(10)	119.9(9)
C(1)-C(2)-C(3)	116.6(8)	C(10)-C(2)-C(3)	123.4(9)
O(2)-C(3)-C(4)	123.7(10)	O(2)-C(3)-C(2)	118.9(9)
C(4)-C(3)-C(2)	117.4(9)	C(9)-C(4)-C(5)	116.9(8)
C(9)-C(4)-C(3)	121.5(9)	C(5)-C(4)-C(3)	121.5(9)
C(6)-C(5)-C(4)	120.5(10)	C(5)-C(6)-C(7)	119.0(11)
C(8)-C(7)-C(6)	123.0(11)	C(7)-C(8)-C(9)	115.8(12)
C(4)-C(9)-O(1)	119.8(7)	C(4)-C(9)-C(8)	124.6(10)
O(1)-C(9)-C(8)	115.4(10)	C(11)-C(10)-C(2)	178.0(11)
C(10)-C(11)-C(12)	178.8(11)	C(13)-C(12)-C(17)	117.2(8)
C(13)-C(12)-C(11)	123.2(9)	C(17)-C(12)-C(11)	119.6(9)
C(14)-C(13)-C(12)	121.1(9)	C(13)-C(14)-C(15)	121.9(10)
O(3)-C(15)-C(14)	117.3(9)	O(3)-C(15)-C(16)	123.8(9)
C(14)-C(15)-C(16)	118.7(9)	C(17)-C(16)-C(15)	117.9(9)
C(16)-C(17)-C(12)	123.0(9)	O(3)-C(18)-C(19)	106.1(8)
O(3)-C(18)-C(20)	109.3(7)	C(19)-C(18)-C(20)	113.1(8)
C(22)-C(21)-O(4)	123.0(8)	C(21)-C(22)-C(23)	120.5(9)
C(21)-C(22)-C(30)	117.4(9)	C(23)-C(22)-C(30)	122.0(9)
O(5)-C(23)-C(22)	124.2(9)	O(5)-C(23)-C(24)	119.0(10)
C(22)-C(23)-C(24)	116.6(10)	C(25)-C(24)-C(29)	118.1(9)
C(25)-C(24)-C(23)	123.0(10)	C(29)-C(24)-C(23)	118.9(9)
C(24)-C(25)-C(26)	119.6(11)	C(27)-C(26)-C(25)	122.2(10)
C(26)-C(27)-C(28)	119.2(10)	C(29)-C(28)-C(27)	118.2(10)
C(28)-C(29)-C(24)	122.7(9)	C(28)-C(29)-O(4)	115.2(9)
C(24)-C(29)-O(4)	122.1(8)	C(31)-C(30)-C(22)	177.8(10)
C(30)-C(31)-C(32)	176.6(9)	C(33)-C(32)-C(37)	118.2(8)
C(33)-C(32)-C(31)	122.5(9)	C(37)-C(32)-C(31)	119.2(9)
C(32)-C(33)-C(34)	121.1(9)	C(35)-C(34)-C(33)	121.2(9)
O(6)-C(35)-C(36)	125.5(9)	O(6)-C(35)-C(34)	115.4(9)
C(36)-C(35)-C(34)	119.0(8)	C(35)-C(36)-C(37)	120.8(9)
C(36)-C(37)-C(32)	119.7(9)	O(6)-C(38)-C(40)	113.2(8)
O(6)-C(38)-C(39)	105.3(9)	C(40)-C(38)-C(39)	112.4(8)

Symmetry transformations used to generate equivalent atoms:

--------End of Electronic Supplementary Information--------