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Pulsed-current versus constant-voltage light-emitting electrochemical cells with trifluoromethyl-substituted cationic iridium(III) complexes

Nail M. Shavaleev,*^a Rosario Scopelliti,^a Michael Grätzel,^a Mohammad K. Nazeeruddin,*^a Antonio Pertegás,^b Cristina Roldan,^b Daniel Tordera,^b Henk J. Bolink*^b

^aLaboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. E-mail: nail.shavaleev@epfl.ch, mdkhaja.nazeeruddin@epfl.ch

^bInstituto de Ciencia Molecular, Universidad de Valencia, C/ Catedrático J. Beltrán 2, ES-46980 Paterna (Valencia), Spain. E-mail: henk.bolink@uv.es

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Single crystals for X-ray analysis were grown by slow evaporation of a mixed CH_2Cl_2 /heptane solution (2) or a CH_2Cl_2 /hexane solution (3) and by vapour diffusion of ether into a concentrated CH_2Cl_2 solution (4). The diffraction data were measured at 100(2) K using Mo K_{α} radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by $EvalCCD^1$ and then corrected for absorption.² The solution and refinement were performed by SHELX.³ The crystal structures were refined using full-matrix least-squares based on F^2 with all non-H atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

compound	2	3	4
empirical formula	C42H38F12IrN4P	C36H22F12IrN4P	C38H26F12IrN4P
fw	1049.93	961.75	989.80
temp [K]	100(2)	100(2)	100(2)
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_{1}/c$	$P2_{1}/c$	Fdd2
unit cell dimensions	a = 13.440(3) Å	a = 10.557(5) Å	a = 19.198(3) Å
	b = 13.5222(13) Å	b = 33.014(10) Å	b = 68.958(10) Å
	c = 26.448(6) Å	c = 10.957(3) Å	c = 11.0075(12) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 91.526(16)^{\circ}$	$\beta = 118.22(2)^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
vol [Å] ³	4804.9(15)	3365.0(19)	14572(4)
Ζ	4	4	16
ρ (calc) [Mg/m ³]	1.451	1.898	1.805
$\mu [\mathrm{mm}^{-1}]$	2.890	4.117	3.806
F(000)	2072	1864	7712
cryst size [mm ³]	$0.45 \times 0.40 \times 0.07$	$0.49 \times 0.42 \times 0.18$	0.34 imes 0.22 imes 0.18
θ range	3.01 – 27.50°	3.25 – 26.54°	3.18 – 27.50°
index ranges	$-17 \le h \le 17$	$-13 \le h \le 12$	$-24 \le h \le 24$
	$-17 \le k \le 17$	$-41 \le k \le 40$	$-89 \le k \le 89$
	$-34 \le l \le 34$	$-13 \le l \le 13$	$-14 \le l \le 14$
reflns collected	52312	46698	62389
independent reflns	10899 [R(int) =	6509 [R(int) =	8011 [R(int) =
	0.0900]	0.0537]	0.0248]
completeness to θ	27.50° – 98.6%	25.00° – 99.8%	27.50° – 99.8%
absorption correction	semi-empirical from	semi-empirical from	semi-empirical from
,	equivalents	equivalents	equivalents
max/min transmission	0.7456 / 0.3690	0.7454 / 0.3552	0.7456 / 0.4778
refinement method	full-matrix least-	full-matrix least-	full-matrix least-
1	squares on F ²	squares on F ²	squares on F ²
data/restraints/params	10899 / 0 / 541	6509 / 119 / 524	8011 / 1 / 506
GOF on F ²	1.080	1.104	1.124 D1 0.01(0 D2
final R indices $[I > 2\sigma(I)]$	R1 = 0.0629, WR2 =	RI = 0.02 / /, WR2 =	R1 = 0.0168, WR2 =
	0.1552 D1 0.0020 D2	0.06/1	0.0359
k indices (all data)	$K_1 = 0.0829, WK2 = 0.1670$	$K_1 = 0.0323, WK2 =$	$K_1 = 0.0181, WK2 =$
-hh-ttttt	0.10/9	0.0703	0.0304
absolute structure parameter			0.021(4)
largest diff. peak/hole [e/Å ³]	4.247 / -2.262	1.876 / -1.411	0.576 / -0.583

Table S1. Crystal Data and Structure Refinement.

2. Electrochemistry

Electrochemical experiments were conducted in DMF (99.8%, Extra Dry, over Molecular Sieves, AcroSeal[®], Acros) or acetonitrile (99.9%, Extra Dry, over Molecular Sieves, AcroSeal[®], Acros), with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Fluka, electrochemical grade) as the supporting electrolyte, with a PC controlled AutoLab PSTAT10 electrochemical workstation.

The experiments were carried out under argon in an electrochemical cell through which a stream of Ar was passed (during the measurement, the flow of Ar was stopped to prevent stirring of the solution). Glassy carbon, platinum spiral, and platinum wire served as working, counter, and quasi-reference⁴ electrodes. Ferrocene was added as an internal reference⁵ at the end of each experiment. Estimated error: ± 50 mV. The anodic/cathodic peak separation for the standard (Fc⁺/Fc couple) at 100 mV/s was 78–83 mV.



Figure S1. Cyclic voltammograms of **1–5** in DMF (GCE, 0.1 M NBu₄PF₆, 100 mV/s). The unit on the vertical axis is 10μ A.

3. Spectroscopy

EPFL, Lausanne: Electronic absorption spectra were recorded with an HP/Agilent 8453 Diode Array UV/VIS spectrophotometer under air in optical cells of 2 or 10 mm path length. The solutions in CH_2Cl_2 (Sigma-Aldrich, puriss p.a., ACS reagent) were freshly prepared before experiment.

The solutions of Ir(III) complexes for photophysical measurements were degassed by bubbling with argon, and were kept in gas-tight Young-tap-modified fluorescence cells. The corrected luminescence spectra were recorded with a HORIBA Jobin Yvon FluoroLog[®]-3 spectrofluorometer at 90° optical geometry. The luminescence quantum yields were calculated from the corrected emission spectra (excitation wavelengths 350 and 360 nm) by comparison with a standard, a solution of quinine hemisulfate salt monohydrate (BioReagent, suitable for fluorescence, >98.0%, Fluka) in 0.5 M H₂SO₄ ($\Phi = 54.6\%$).⁶ The following values of the refractive indices were used for the calculations of Φ : 1.333 for 0.5 M H₂SO₄ and 1.4242 for CH₂Cl₂. Excited-state lifetimes were measured on the same spectrofluorometer with a HORIBA NanoLED (406 nm) excitation source.

Universidad de Valencia, Valencia: The photoluminescence spectra and quantum yields of 1–5 in thin films [1–5 and 1-butyl-3-methylimidazolium hexafluorophosphate (>98.5%, Sigma-Aldrich) in a 4 to 1 molar ratio] were measured with a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System under air ($\lambda_{exc} = 315$ nm). Thin films were prepared on quartz substrates by spin-coating from a solution.

Table S2. UV-Vis Absorption Maxima.^a

Complex	$\lambda_{\rm abs}/\rm{nm}~(\epsilon/10^3~\rm{M}^{-1}~\rm{cm}^{-1})$
1	256 (59), 332 (9.9)
2	256 (60), 334 (10)
3	265 (58), 368 (7.4)
4	266 (65)
5	255 (58), 269 (58), 282 (57), 328 (23), 378 (12)

^{*a*} At (6.82–9.40)×10⁻⁵ M in dichloromethane at room temperature, 250–800 nm. Errors: ± 2 nm for λ_{abs} ; $\pm 5\%$ for ε .



Figure S2. Absorption spectra of **1–5** at $(6.82–9.40)\times10^{-5}$ M in dichloromethane. The unit on the vertical axis is 10×10^3 M⁻¹ cm⁻¹. The spectra are shifted along the vertical axis by 10×10^3 M⁻¹ cm⁻¹.



Figure S3. Normalized phosphorescence excitation spectra of **1**–**5** at 10^{-5} M in argon-saturated dichloromethane at room temperature (the emission was monitored at the maximum of the luminescence band; $\Delta \lambda_{exc} = 1$ nm). The solutions were optically dense below 310 nm. The spectra are shifted along the vertical axis.



Figure S4. Luminescence decay of **1**–**5** at 10^{-5} M in argon-saturated dichloromethane at room temperature ($\lambda_{exc} = 406$ nm; $\lambda_{em} = 520$, 550 nm). Experimental data (black) and a single exponential fit to the data (red).



Figure S4. (continued)



Figure S4. (continued)

4. Electroluminescence



Figure S5. Time-dependence of normalized luminance, current, efficacy, powerefficiency and EQE of a constant-voltage (4 V) LEC device ITO/PEDOT:PSS/1– **5**:BMIM–PF₆ (4:1; 100 nm)/Al. The peak parameters are listed in Table 3. The normalized time-dependencies of E, η and EQE coincide.



Figure S5. (continued)



Figure S6. Time-dependence of normalized luminance, voltage, efficacy, powerefficiency and EQE of a pulsed-current LEC device ITO/PEDOT:PSS/**1–5**:BMIM– PF₆ (4:1; 100 nm)/Al (block wave, 1000 Hz; duty cycle 50%; 100 A m⁻² per pulse; 50 A m⁻² average). The peak parameters are listed in Table 3. The normalized timedependencies of *E* and EQE coincide.



Figure S6. (continued)

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LEC	Voltage/V		
	$V_{\max}{}^{b}$	$(L/E/\eta/EQE)_{max}$	$L_{1/2}$
1	4.5	3.0	2.8
2	4.8	3.6	3.0
3	4.1	2.9	2.8
4	4.8	3.0	2.8
5	5.3	2.7–2.9	2.5

Table S3. Voltage in $PCLEC^a$

^{*a*} ITO/PEDOT:PSS/**1–5**:BMIM–PF₆ (4:1; 100 nm)/Al. PCLEC; block wave, 1000 Hz; duty cycle 50%; 100 A m⁻² per pulse; 50 A m⁻² average.

^b The maximum voltage (V_{max}) required at the start.

 Table S4. Average Current per Pulse in PCLEC^a

LEC	$I/A \text{ m}^{-2}$	$2\sigma/\mathrm{A~m}^{-2}$
1	100	3
2	101	5
3	101	2
4	101	2
5	100	3

^{*a*} ITO/PEDOT:PSS/**1–5**:BMIM–PF₆ (4:1; 100 nm)/Al. PCLEC; block wave, 1000 Hz; duty cycle 50%; 100 A m⁻² per pulse; 50 A m⁻² average.

^{*b*} Average current per pulse (*I*) and sample standard deviation, σ , were calculated with AVERAGE and STDEV functions of Microsoft Excel.

Table S5. Luminance of LEC (and its Ratio to the Peak Luminance) at the Peak Efficiency (E, η, EQE)

$L/cd m^{-2} (\boldsymbol{L}/\boldsymbol{L}_{max})$		
LEC	CV	PC
1	142 (0.23)	477 (0.98)
2	137 (0.32)	852 ^{<i>a</i>} (1.0)
		834 ^b (0.98)
3	250 (0.49)	518 (1.0)
4	60 (0.21)	195 (1.0)
5	682 (0.62)	452 ^{<i>a</i>} (1.0)
		435 ^{<i>b</i>} (0.96)

^{*a*} $L(E_{\text{max}}, \text{EQE}_{\text{max}}).$

^b $L(\eta \max)$.

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¹H NMR Spectrum of 1 in CD_2Cl_2 (top, complete; bottom, arom. H).



¹H NMR Spectrum of 2 in CD_2Cl_2 (top, complete; bottom, arom. H).



¹H NMR Spectrum of 3 in CD₂Cl₂.



¹H NMR Spectrum of 4 in CD_2Cl_2 (top, complete; bottom, arom. H).





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¹H NMR Spectrum of 5 in CD₂Cl₂.



 ^{19}F NMR Spectrum of 1 in $\rm CD_2Cl_2.$



¹⁹F NMR Spectrum of 2 in CD₂Cl₂.





 ^{19}F NMR Spectrum of 4 in CD₂Cl₂.



 ^{19}F NMR Spectrum of 5 in CD₂Cl₂.