

graphic image from which the FFT was calculated. FFT images correspond to the module of two-dimensional (2D)-FFT (displayed in linear scale), calculated by using the WSxM software developed by R. Fernández et al. [19].

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Highly Efficient Red Electrophosphorescent Devices Based on Iridium Isoquinoline Complexes: Remarkable External Quantum Efficiency Over a Wide Range of Current**

By Ying-Ju Su, Heh-Lung Huang, Chien-Le Li, Chin-Hsiung Chien, Yu-Tai Tao,* Pi-Tai Chou, Swarup Datta, and Rai-Shung Liu*

Organic light-emitting devices (OLEDs) hold great potential for application in flat-panel displays due to rapid progress in material design and device fabrication in recent years.^[1–4] Red, green, and blue emissions of matching efficiencies are

required for a full-color display. Greater success has been achieved in the development of a green emitter than that of red one in both fluorescent and phosphorescent displays. For example, devices based on green fluorescent dopant C545T^[5] can reach a luminance efficiency > 10 cd A^{−1}. In contrast, the best red OLEDs reported^[6–10] can only reach ~3 cd A^{−1} and external quantum efficiencies less than 1 %. OLEDs based on phosphorescent materials^[11] can significantly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100 %. Unfortunately, most of phosphorescent emitters have a long lifetime (> 10 μs), which results in saturation of emissive sites at increasing currents. The first red phosphorescent material was reported for complexes of the type EuL₃, where L denotes a ligand.^[12] The long lifetime of the electronically excited europium(III) (350 μs) leads to dominant triplet–triplet (T–T) annihilation at high currents, and the maximum efficiency is only 1.4 %. Although platinum(II) octaethylporphyrin (PtOEP) doped into 4,4,N,N'-dicarbazole-biphenyl (CBP) shows an external quantum efficiency η_{ext} = 5.6 %, for a red phosphor,^[4,13] the occurrence of T–T annihilation is inevitable at high currents (η_{ext} = 0.5 % at 100 mA cm^{−2}) due to its relatively long phosphorescent lifetime (50–80 μs). Recently, a more efficient red phosphor has been reported, Ir(btp)₂(acac)^[14] (btp = 2-(2'-benzo[4.5-a]thienyl)pyridinato; acac = acetylacetonate), that achieved an efficiency of η_{ext} = 7.0 % at low current. The relatively short phosphorescent lifetime (4 μs) significantly improves the external efficiency at high currents (η_{ext} = 2.5 % at 100 mA cm^{−2}). A short phosphorescence lifetime is crucial for the performance of a phosphorescent material, particularly its maximum brightness and efficiency at high currents. In this communication, we wish to report a series of efficient red phosphorescent emitters based on iridium 1-(phenyl)isoquinoline complexes which show strong electroluminescence (EL) brightness and efficiency, even at high currents.

Scheme 1 outlines the synthetic protocol for red phosphorescent complexes: Ir(piq)₂(acac), Ir(piq-F)₂(acac), and Ir(piq-F)₃, with piq and piq-F representing the 1-(phenyl)isoquinoline and 2-(4'-fluorophenyl)isoquinoline ligands, respectively. The *para*-fluoro substituent of Ir(piq-F)₂(acac) and Ir(piq-F)₃ is used to tune emission wavelength without loss of performance efficiency.^[15] 1-(Phenyl)isoquinoline ligand was prepared from the reaction of isoquinoline with the corresponding phenyl magnesium bromide. The complexes Ir(piq)₂(acac) and Ir(piq-F)₂(acac) were prepared via treatment of diiridium precursors^[16] with acetylacetone in the presence of Na₂CO₃. The tris-chelated complex Ir(piq-F)₃ was obtained from heating the diiridium complexes with AgCF₃SO₃ in the presence of a five-fold amount of piq-F at 200 °C for 24 h. We also prepared complex with an iridium center cyclometalated with a 5-(4'-fluorophenyl)-(3,4-benzoquinoline) ligand, Ir(pbq-F)₂(acac), which is expected to show red-shifted EL. ¹H and ¹³C NMR, IR, mass, and elemental analyses are consistent with the proposed structures.

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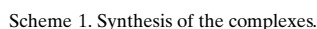


Table 1. Photophysical data of iridium complexes.

[a] Data obtained in CH₂Cl₂. [b] Lifetime measured in solid film.

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deduced to be as short as 3.6–16.4 μs (see Table 1), which correlates well with the unusually large extinction coefficients measured for the $^3\text{MLCT}$ bands.

OLEDs using iridium complexes were fabricated by high-vacuum (10^{-6} torr) thermal evaporation onto pre-cleaned glass substrates. Figure 2 shows the configuration of the devices, in which CBP acted as a host material for the com-

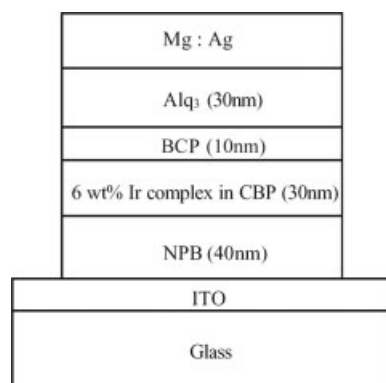


Fig. 2. Configuration of the devices used, including typical layer thicknesses.

plexes, bathocuproine (BCP) as a hole blocker, and 4,4'-bis[*N*-(naphthyl)-*N*-phenyl-amino]biphenyl (NPB) and tris-(8-hydroxyquinoline)aluminum(III) (Alq_3) as a hole-transport layer and an electron-transport layer, respectively.

All four devices exhibited bright orange-red to orange emissions, which were independent of the applied voltages from 6 V to 12 V. Figure 3 shows the EL spectra of devices based on these four iridium species at a current density of $J = 20 \text{ mA cm}^{-2}$. The corresponding CIE (Commission Internationale de l'Eclairage) coordinates are $x = 0.68$, $y = 0.32$ for $\text{Ir}(\text{piq})_2(\text{acac})$, $x = 0.61$, $y = 0.36$ for $\text{Ir}(\text{piq-F})_2(\text{acac})$, $x = 0.61$, $y = 0.38$ for $\text{Ir}(\text{piq-F})_3$, and $x = 0.65$, $y = 0.33$ for $\text{Ir}(\text{pbq})_2(\text{acac})$, respectively (see Table 2).

Using the above devices, EL data for the complexes were acquired, as summarized in Table 2. Complexes $\text{Ir}(\text{piq})_2(\text{acac})$, $\text{Ir}(\text{piq-F})_2(\text{acac})$, and $\text{Ir}(\text{piq-F})_3$ show better performance than $\text{Ir}(\text{pbq})_2(\text{acac})$ in both maximum brightness and quantum efficiency. Using $\text{Ir}(\text{piq-F})_2(\text{acac})$, a maximum brightness of 27130 cd m^{-2} was achieved at a current density of $J = 400 \text{ mA cm}^{-2}$. The external quantum efficiency η_{ext} of $\text{Ir}(\text{piq-F})_2(\text{acac})$ was 8.67 % at $J = 20 \text{ mA cm}^{-2}$, where a maximum of luminance efficiency (LE) of 4.73 lm W^{-1} and a power efficiency (PE) of 13.7 cd A^{-1} were obtained (see Fig. 4). The external quantum efficiency decreased very slowly with increasing current. At $J = 100 \text{ mA cm}^{-2}$, the value of η_{ext} remained as high as 6.84 %, with a luminance and power efficiency 2.83 lm W^{-1} and 10.8 cd A^{-1} respectively. At high current $J = 400 \text{ mA cm}^{-2}$, η_{ext} was still as high as

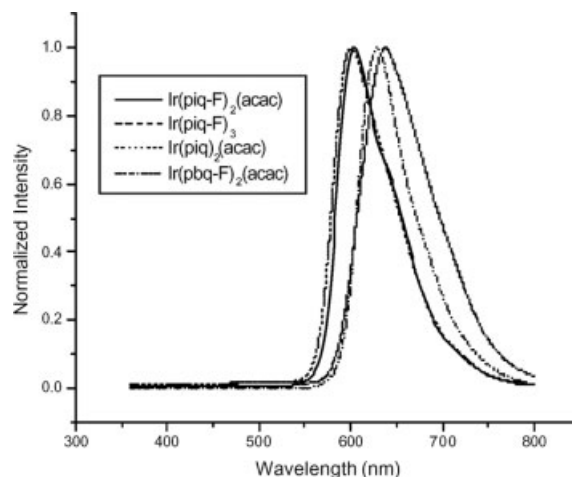


Fig. 3. EL spectra of four iridium species at $J = 20 \text{ mA cm}^{-2}$.

4.20 %, with $\text{LE} = 1.42 \text{ lm W}^{-1}$ and $\text{PE} = 6.75 \text{ cd A}^{-1}$. In comparison, the maximum brightness of a known complex $\text{btp}_2\text{Ir}(\text{acac})$ ^[14] was reported to be only ca. 6800 cd m^{-2} at $J = 690 \text{ mA cm}^{-2}$ in spite of its external quantum efficiency of $\eta_{\text{ext}} = 7.0$ at $J = 0.01 \text{ mA cm}^{-2}$. The η_{ext} value for $\text{btp}_2\text{Ir}(\text{acac})$ also drops more quickly with its increasing current, $\eta_{\text{ext}} = 4.4$ and 1.3 at $J = 20$ and 400 mA cm^{-2} respectively. The data in Table 2 reveal that $\text{Ir}(\text{piq})_2(\text{acac})$ and $\text{Ir}(\text{piq-F})_3$ are equally efficient as $\text{Ir}(\text{piq-F})_2(\text{acac})$ in terms of maximum brightness, power, luminance, and external quantum efficiency. The role of the *para*-fluoro substituent of $\text{Ir}(\text{piq-F})_2(\text{acac})$ and $\text{Ir}(\text{piq-F})_3$ is to tune the luminance towards high frequency without loss of EL efficiency. One notable feature for $\text{Ir}(\text{piq})_2(\text{acac})$ is the exceptionally high external quantum efficiency $\eta_{\text{ext}} = 7.00$ at $J = 400 \text{ mA cm}^{-2}$, corresponding to a loss of only 28 % from its maximum value $\eta_{\text{ext}} = 9.71$ at $J = 38 \text{ mA cm}^{-2}$.

In summary, we have reported a series of high-efficiency and high-brightness red phosphors based on iridium complexes bearing a 1-(phenyl)isoquinoline framework.^[19] All studied complexes exhibit prominent EL emission in the range 600–630 nm. Unlike normal iridium phosphor complexes, remarkably high efficiency can be maintained at high currents with a

Table 2. Electrophosphorescence data for iridium complexes.

Parameter	Brightness [cd m^{-2}]	EQE [%]	PE [cd A^{-1}]	LE [lm W^{-1}]	Voltage [V]	CIE corordinates
$\text{Ir}(\text{piq})_2(\text{acac})$	1514 [a]	8.46	7.56	2.78	8.53	$x = 0.68$
	8224 [b]	9.21	8.22	2.34	11.01	$y = 0.32$
	24978 [c]	7.00	6.08	1.88	13.92	
$\text{Ir}(\text{piq-F})_2(\text{acac})$	2744	8.67	13.72	4.73	9.11	$x = 0.61$
	10808	6.84	10.82	2.82	12.01	$y = 0.36$
	26947	4.27	6.75	1.42	14.91	
$\text{Ir}(\text{piq-F})_3$	2078	5.81	10.36	3.80	8.56	$x = 0.61$
	9625	5.41	9.66	2.80	10.83	$y = 0.38$
	25970	3.65	6.50	1.51	13.60	
$\text{Ir}(\text{pbq-F})_2(\text{acac})$	841	5.63	4.20	1.52	8.66	$x = 0.65$
	3788	5.10	3.80	1.08	11.12	$y = 0.33$
	10734	3.66	2.65	0.60	13.93	

For each parameter, the data in different rows correspond to those measured at different current densities: [a] $J = 20 \text{ mA cm}^{-2}$. [b] $J = 100 \text{ mA cm}^{-2}$. [c] $J = 400 \text{ mA cm}^{-2}$.

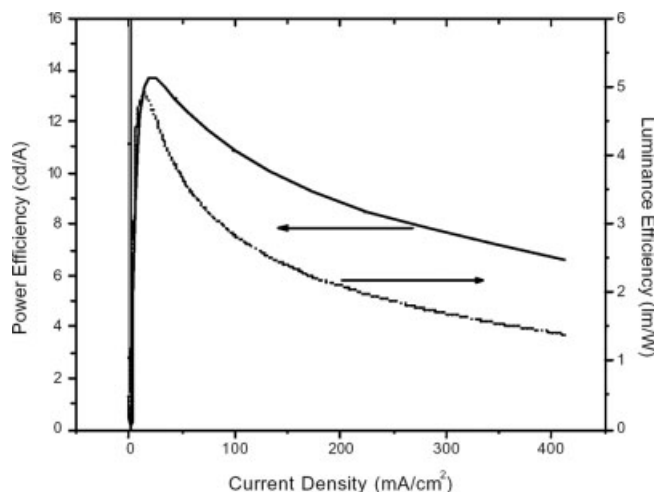


Fig. 4. Power and luminance efficiencies as function of current density of the Ir(piq-F)₂(acac) device.

negligible effect from either the T-T annihilation or saturation of the excited state. Such an outstanding performance is related to the iridium isoquinoline framework because iridium complexes bearing a 3-(phenyl)isoquinoline ligand show an efficient yellow phosphorescent emission.^[20] Characterization of these iridium-isoquinoline complexes to understand the reason behind their remarkable photophysical properties is under investigation.

Experimental

1-(Phenyl)isoquinoline (piq): To a diethyl ether solution (12 mL) of isoquinoline was added phenylmagnesium bromide (2.5 M in THF, 2.55 mL) at 23 °C, and the mixture was stirred for 36 h before treatment with NH₄Cl solution (10 mL). The diethyl ether layer was separated, concentrated, and eluted through a silica column to afford 1-(phenyl)isoquinoline as a colorless solid (0.54 g, 2.63 mmol, 41 %). IR (Nujol) [cm⁻¹]: 2960(m), 2922(m), 2866(m), 2853(m), 1577(s), 1541(s), 1394(s), 1350(s), 1188(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: δ 8.58 (d, *J* = 6 Hz 1H); 8.09 (d, *J* = 8 Hz 1H); 7.86 (d, *J* = 8 Hz 1H); 7.68 (d, *J* = 6.8 Hz 1H); 7.63 (t, *J* = 5.2 Hz 1H); 7.51 (m, 1H). ¹³C NMR (CDCl₃, 400 MHz) [ppm]: δ 160.4, 142.2, 136.8, 129.9, 129.9, 128.53, 128.3, 127.5, 127.1, 126.9, 126.6, 119.8.

1-(4'-Fluorophenyl)isoquinoline (piq-F): This compound was prepared similarly to the procedure described for the piq ligand from isoquinoline and 4-fluorophenylmagnesium bromide, and 2-(4'-fluorophenyl)isoquinoline was obtained as a colorless solid in 50 % yield. IR (Nujol) [cm⁻¹]: 2962(m), 2921(m), 2865(m), 2852(m), 1576(s), 1540(s), 1393(s), 1351(s), 1188(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: δ 8.58 (d, *J* = 6.0 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.64–7.72 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 8 Hz, 2H). ¹³C NMR (CDCl₃, 400 MHz) [ppm]: δ 162.9 (d, *J*_{C-F} = 246.6 Hz), 159.4, 141.9, 131.6 (d, *J*_{C-F} = 8.4 Hz), 129.9, 127.0, 126.9, 126.4, 119.9, 115.1 (d, *J*_{C-F} = 21.4 Hz). High-resolution mass spectrometry (HRMS) (70 eV, electron impact (EI)): Calcd. for C₁₅H₁₀NF: 223.0797. Found C₁₅H₁₀NF: 223.0795.

5-(4'-Fluorophenyl)-(3,4-benzoquinoline) (pbq-F): This compound was prepared similarly to the procedure described for the piq ligand above from 3,4-benzoquinoline (3.00 g, 16.7 mmol) and 4-fluorophenylmagnesium bromide (25.1 mmol), and colorless solid was obtained in 87 % yield after purification from a silica column. To a CHCl₃ solution (50 mL) of this solid (4.00 g, 14.6 mmol) was added MnO₂ (40 g) at 23 °C, and the mixtures were stirred for 24 h. The solution was filtered, and the filtrate was concentrated, then purified on a silica column to afford 5-(4'-fluorophenyl)-(3,4-benzoquinoline) as a colorless solid (3.70 g, 13.5 mmol). IR (Nujol) [cm⁻¹]: 2960(m), 2920(m), 2864(m), 2853(m), 1577(s), 1541(s), 1394(s), 1350(s), 1188(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.77–7.66 (m, 4H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (CDCl₃,

100 MHz) [ppm]: δ 162.9 (d, *J*_{C-F} = 245.8 Hz), 159.7, 143.4, 135.6, 133.1, 131.5, 131.4, 130.3, 130.0, 128.6, 128.2, 126.9, 126.8, 124.7, 123.4, 122.0, 121.7, 115.3, 115.1; HRMS (70 eV, EI): Calcd for C₁₉H₁₂FN: 273.3045. Found: 273.3043.

Ir(piq)₂(acac): To a mixed solvent of ethoxyethanol (9.0 mL) and water (3 mL) was added IrCl₃·nH₂O (0.69 g, 84.7 wt.-% Ir content) and piq (1.00 g, 4.88 mmol), and the mixture was heated at 130 °C for 24 h. The resulting orange solution was concentrated at 60 °C under vacuum and the remaining orange solid was collected by filtration, washed with water, hexane, and finally with diethyl ether. The weight of this solid was 1.15 g (0.90 mmol, 92 %). To an ethoxyethanol (12 mL) of this solid (1.0 g, 0.79 mmol) was added acetylacetone (0.58 mL) and Na₂CO₃ (410 mg), and the mixture was heated at 100 °C for 24 h. The resulting red solution was concentrated at 60 °C under vacuum and the residues were eluted through a silica column to afford Ir(piq)₂(acac) as a red solid (0.30 g, 0.42 mmol, 28 %). IR (Nujol) [cm⁻¹]: 2964(m), 2920(m), 2866(m), 2851(m), 1574(s), 1542(s), 1390(s), 1351(s), 1188(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: δ 8.97 (d, *J* = 9.2 Hz, 2H); 8.44 (d, *J* = 6.8 Hz, 2H); 8.18 (d, *J* = 8.0 Hz 2H); 7.91 (m, 1H); 7.69 (m, 1H); 7.45 (d, *J* = 6.4 Hz 1H); 6.87 (t, *J* = 6.4 Hz 1H); 6.37 (d, *J* = 7.2 Hz 1H); 5.18 (s, 1H); 1.74 (s, 6H). ¹³C NMR (CD₂Cl₂, 400 MHz) [ppm]: δ 185.30, 169.13, 151.98, 147.23, 140.82, 137.64, 133.98, 121.17, 130.10, 129.12, 128.22, 127.69, 126.97, 126.71, 120.85, 150.60, 100.89, 28.68. Anal. calcd. for C₃₅H₂₇IrF₂N₂O₂: C, 60.07; H, 3.89; N, 4.00. Found: C, 59.89; H, 3.78; N, 3.89.

Ir(piq-F)₂(acac): This compound was prepared from 1-(4'-fluorophenyl)isoquinoline (piq-F) and IrCl₃·nH₂O according to the procedure described for Ir(piq)₂(acac). IR (Nujol) [cm⁻¹]: 2952(m), 2926(m), 2853(m), 2853(m), 1575(s), 1507(s), 1456(s), 1270(s). ¹H NMR (CD₂Cl₂, 400 MHz) [ppm]: δ 8.90 (dd, *J* = 4.8, 2.4 Hz, 2H); 8.35 (d, *J* = 5.2 Hz, 2H); 8.24 (dd, *J* = 7.2, 4.2 Hz, 2H); 7.98 (dd, *J* = 4.4, 3.0 Hz 2H); 7.74–7.77 (m, 4H), 7.55 (d, *J* = 5.2 Hz, 2H), 6.66 (td, *J* = 8.0, 2.0 Hz, 2H), 5.96 (dd, *J* = 7.6, 2.0, 2H), 5.27 (s, 1H), 1.77 (s, 6H). ¹³C NMR (CD₂Cl₂, 400 MHz) [ppm]: δ 185.4, 168.0, 162.7 (d, *J*_{C-F} = 203.1 Hz), 155.2 (d, *J*_{C-F} = 4.4 Hz), 143.37, 140.47, 137.72, 131.66 (d, *J*_{C-F} = 7.1 Hz), 131.38, 128.46, 127.78, 126.68, 126.42, 120.60, 119.66 (d, *J* = 13.4 Hz), 108.06 (d, *J* = 18.6 Hz), 100.96, 28.62. Anal. calcd for C₃₅H₂₅IrF₂N₂O₂: C, 57.13; H, 3.42; N, 3.81. Found: C, 57.01; H, 3.33; N, 3.66.

Ir(pbq-F)₂(acac): This compound was prepared from 5-(4'-fluorophenyl)-(3,4-benzoquinoline) (pbq-F) and IrCl₃·nH₂O according to the procedure described for the complex Ir(piq-F)₂(acac). IR (Nujol) [cm⁻¹]: 2961(m), 2940(m), 2848(m), 2850(m), 1572(s), 1514(s), 1453(s), 1266(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: δ 9.01 (d, *J* = 8.8 Hz, 2H), 8.67 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 7.6 Hz, 2H), 8.31 (d, *J* = 8.0 Hz, 2H), 8.19 (dd, *J* = 5.6 Hz, *J* = 8.8 Hz, 2H), 7.90 (t, *J* = 7.6 Hz, 2H), 7.78 (t, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 6.73 (dt, *J* = 3.2 Hz, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 3.2 Hz, *J* = 9.6 Hz, 2H), 4.43 (s, 1H), 1.28 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) [ppm]: δ 185.3, 172.0, 161.8 (d, *J*_{C-F} = 245.8 Hz), 155.4, 145.0, 143.9, 133.7, 133.1, 133.0, 131.5, 129.1, 128.9, 127.1, 126.3, 124.7, 123.3, 123.1, 122.6, 122.4, 121.8, 99.9, 27.7. Anal. calcd for C₄₃H₂₉F₂IrN₂O₂: C, 61.78; H, 3.50; N, 3.35. Found: C, 61.77; H, 3.44; N, 3.40.

Ir(piq-F)₃: To a Pyrex tube charged with diiridium complex (300 mg, 0.223 mmol), piq-F (498 mg, 2.23 mmol) and AgCF₃SO₃ (115 mg, 0.48 mmol) were added, and the mixture heated at 200 °C for 24 h. The resulting solid was purified on a silica column to afford Ir(piq-F)₃ as a red solid (40 mg, 0.047 mmol, 21 %). IR (Nujol) [cm⁻¹]: 2944(m), 2924(m), 2860(m), 2850(m), 1574(s), 1500(s), 1444(s), 1268(s). ¹H NMR (CDCl₃, 400 MHz) [ppm]: 8.85–8.86 (m, 3H); 8.15 (dd, *J* = 7.2, 4.4 Hz, 3H), 7.70–7.73 (m, 3H), 7.63–7.65 (m, 6H), 7.27 (d, *J* = 5.2 Hz 3H), 7.11 (d, *J* = 2.4 Hz 3H), 6.67 (td, *J* = 7.2, 2.4 Hz, 3H), 6.58 (dd, *J* = 8.0, 2.0 Hz, 3H). ¹³C NMR (CDCl₃, 400 MHz) [ppm]: δ 167.2 (d, *J* = 4.5 Hz), 166.5, 163.9 (d, *J*_{C-F} = 203.2 Hz), 141.3, 139.54, 136.6, 131.7 (d, *J*_{C-F} = 7.1 Hz), 130.4, 127.7, 127.4, 127.1, 126.3, 122.4 (d, *J*_{C-F} = 13.3 Hz), 120.20, 107.28 (d, *J*_{C-F} = 17.8 Hz). Anal. calcd for C₄₅H₂₇IrF₃N₃: C, 62.93; H, 3.17; N, 4.89. Found: C, 62.88; H, 3.10; N, 4.77.

Measurement of Lifetime and Quantum Yields: Steady-state absorption and emission spectra were recorded by a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. Both wavelength-dependent excitation and emission response of the fluorimeter have been calibrated. A configuration of front-face excitation was used to measure the emission of the solid sample, in which the cell was made by assembling two edge-polished quartz plates with various Teflon spacers. A combination of appropriate filters was used to avoid the interference from the scattered light.

Lifetime studies were performed by an Edinburgh FL 900 photon-counting system with a hydrogen-filled/or a nitrogen lamp as the excitation source. Data were analyzed using the nonlinear least-squares procedure in combination with an iterative convolution method [21]. Single exponential emission decay was obtained for all studied compounds.

Quinine sulfate/1.0 N H₂SO₄ was used as a reference, assuming a fluorescence quantum yield of 0.564 with 360 nm excitation [1], to determined quantum yields of the studied compounds in solution. Solution samples were degassed by three freeze-pump-thaw cycles under vigorous stirring.

OLED Fabrication and Measurements: Pre-patterned indium tin oxide (ITO) substrates with an effective individual device area of 3.14 mm^2 were cleaned by sonication in a detergent solution for 3 min and then washed with large amount of doubly distilled water. Further sonication in ethanol for 3 min followed before blowing dry with a stream of nitrogen. The ITO substrates were then treated with O_2 plasma for one minute before being loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of $0.1\text{--}0.3 \text{ nm s}^{-1}$ under a pressure of $\sim 2 \times 10^{-5}$ torr in an Ulvac Cryogenic deposition system. An alloy of Mg and Ag (ca. 10:1, 50 nm) was deposited as the cathode, which was capped with 100 nm of Ag. The current–voltage–luminance was measured in ambient with a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with 818ST silicon photodiode

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Cell-Responsive Synthetic Hydrogels**

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An important part of tissue function relies on the dynamic dialog that exists between cells and their extracellular matrices (ECM): the ECM is active, presenting bound adhesion sites that interact with cell-surface receptors,^[1] and it is responsive to signals presented by cells, locally degrading under the influence of proteases at the surface of the migrating cell.^[2–4] While artificial biomaterial matrices used in cell culture and tissue engineering have been developed to be responsive to physical^[5–9] and even biochemical^[10–14] stimuli, they do not widely address this concept of responsiveness to cellular stimuli. We mimicked these features in synthetic hydrogel networks, for application in both cell biology and tissue engineering,^[15–17] incorporating pendant receptor-binding sites so that cells can exert traction^[18] and crosslinking protease-sensitive degradation sites so that cells can create a path to enable forward movement.^[19] Our results demonstrate that synthetic materials can be responsive to cellular influences in vitro and in vivo, including here, as an example, inducing and responding to angiogenic invasion.

We formed polymer networks in situ using conjugate addition reactions. We linked molecular building blocks performing either structural (poly(ethylene glycol), PEG) or biological (oligopeptides) function (Scheme 1). Vinyl sulfone (VS)-functionalized multiarmed telechelic PEG macromers reacted with thiolate groups of cysteine-containing peptides by conjugate addition,^[20] a reaction that is highly selective versus biological amines^[21] and can be carried out at physiological temperature and near physiological pH.

We selected PEG-based macromers as the main structural component due to their hydrophilicity and resistance to protein adsorption.^[22,23] We chose bis-cysteine peptides as one biological component, since upon reaction they become part of a crosslinked network structure and contribute to its mechanical character, i.e., elastically active. As a result, any designed sensitivity of these building blocks to cellular proteases

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