

Supplementary Information

Effect of donor structure in new D- π -A systems based on indolo[3,2,1-jk]carbazoles on thermal, electrochemical, optoelectronic and luminescence properties

Grażyna Szafraniec-Gorol^{a*}, Aneta Slodek^a, Dawid Zych^b, Marharyta Vasylieva^c, Mariola Siwy^c, Karolina Sulowska^d, Sebastian Maćkowski^d, Ilya Taydakov^e, Dmitry Goriachiy^c and Ewa Schab-Balcerzak^{a,c}

^a Institute of Chemistry, University of Silesia, 9th Szkolna Street, 40-006 Katowice, Poland

^b Wrocław School of Information Technology, 4 ks. M. Lutra Street, 54-239 Wrocław, Poland

^c Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowska Street, 41-819 Zabrze, Poland

^d Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, 5th Grudziadzka St., 87-100 Torun, Poland

^e P.N. Lebedev Physical Institute, Russian Academy of Sciences, 53 Leninsky Prospect, 119991, Moscow, Russian Federation

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Experimental Materials

All chemicals and starting materials were commercially available and were used without further purification. Solvents were distilled as per the standard methods and purged with nitrogen before use. All reactions were carried out under argon atmosphere unless otherwise indicated. Column chromatography was carried out on Merck silica gel. Thin layer chromatography (TLC) was performed on silica gel (Merck TLC Silica Gel 60). Electrochemical measurements were made in 0.5 mM concentrations for all the cyclic voltammetry measurements. For UV-VIS spectroscopy and ESR spectroscopy was used 0.5 mM concentration of compounds. Electrochemical studies were conducted in 0.1 M solutions of Bu₄NPF₆, 99% (Sigma Aldrich) in dichloromethane (DCM) solvent, CHROMASOLV1, 99.9% (Sigma Aldrich) at room temperature. UV-Vis spectroelectrochemical measurements were performed on the ITO (Indium Tin Oxide) quartz glass working electrode.

Measurements

Spectroscopy

The NMR spectra were recorded on a Bruker Avance 500 MHz instrument by using CDCl_3 as solvent. The steady-state emission and excitation spectra were measured for dichloromethane (CH_2Cl_2) solutions and on the FLS-980 spectrophotometer in ambient temperature using 450W Xe arc lamp as a light source and PMT (Hamamatsu, R928P) in cooled housing as a detector. The emission and excitation spectra were measured by using spectrophotometer Hitachi F-7000. The quantum yields of fluorescence (Φ) were determined by absolute method in room temperature, using the integrating sphere with solvent as a blank. The time-resolved measurement has been prepared at optically diluted solutions at room temperature using the time correlated single photon counting methods on the FLS-980 Edinburgh Instruments. Excitation wavelengths were obtained using the picosecond pulsed diode EPL-375 nm with 100 ns pulse period as light sources with voltage of 5 mV, depending on the obtained excitation maxima. PMT (Hamamatsu, R928P) in cooled housing was used as a detector. The system was alignment at emission wavelengths. Additionally for the analysis of a fluorescence decay, an instrument response function needs to be obtained. The IRF contains the information about the time response of the overall optical and electronic system. The IRF was designate using ludox solution as a standard at 375 nm. The influences of the Raman scattering of solvent on emission of sample was avoided using filter.

Electrochemistry

The electrochemical cell comprised of the platinum electrode with a 1 mm diameter of Pt as a working electrode, an $\text{Ag}|\text{Ag}^+$ electrode as a pseudoreference electrode and a platinum coil as an auxiliary electrode. Measurements were conducted at room temperature at a potential rate of 50 mV/s and were calibrated against a ferrocene/ferrocenium redox couple. Electrochemical measurements were conducted in 1.0 mM concentrations of all compounds for all cyclic voltammetry measurements. Electrochemical studies were undertaken in 0.1 M solutions of Bu_4NBF_4 , 99% (Sigma Aldrich) in dichloromethane (DCM) CHROMASOLV®, 99.9% (Sigma Aldrich). UV- Vis-NIR spectroscopy and spectroelectrochemistry were performed on HP 8453 apparatus. In situ EPR spectroelectrochemical experiments were taken using a JES- FA 200 (JEOL) spectrometer.

OLED fabrication and testing

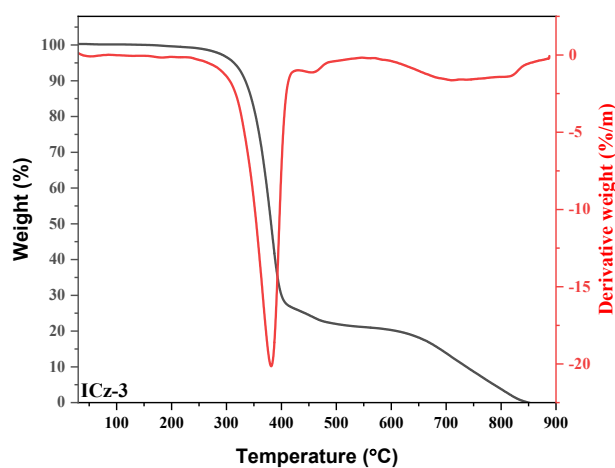
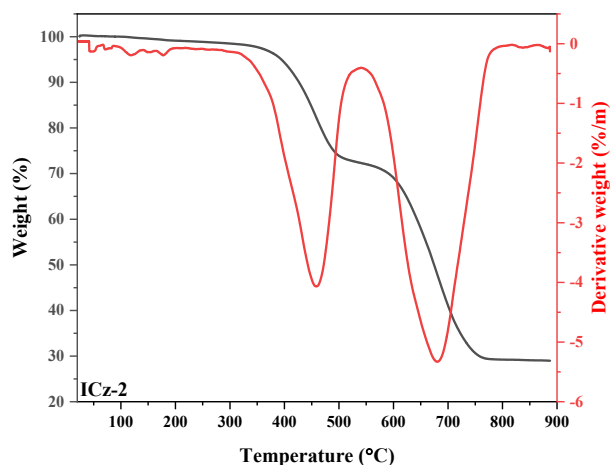
OLEDs with sandwich configuration ITO/PEDOT:PSS/compound/Al and ITO/PEDOT:PSS/compound/:PVK:PBD/Al with 2 and 15 wt. % of molecule content in the blend were fabricated. Devices were prepared on OSSILA substrates with pixilated ITO anodes, cleaned with detergent, deionized water, 10% NaOH solution, water and isopropyl alcohol in the ultrasonic bath. Substrates were covered with PEDOT:PSS film by spin coating at 5000 rpm for 60 s and annealed for 5 min at 120°C. The active layer was spin-coated on top of the PEDOT:PSS layer from chloroform solution (10 mg/mL) at 1000 rpm for 60 s and annealed for 5 min at 100°C. Finally, Al was vacuum-deposited at a pressure of $5 \cdot 10^{-5}$ Torr. Electroluminescence (EL) spectra were measured with the voltage applied using a precise voltage supply (GwInstek PSP-405) and the sample was fixed to an XYZ stage. Light from the OLED device was collected through a 30mm lens, focused on the entrance slit (50 μm) of a monochromator (Shamrock SR-303i) and detected using a CCD detector (AndoriDus 12305). Typical acquisition times were equal to 10 seconds. The pre-alignment of the setup was done using a 405 nm laser. The active layers thickness was measured using atomic force microscopy (AFM) using TopoMetrix Explorer device (Industriële Veiling Eindhoven B.V., CA Eindhoven, The Netherlands), operating in contact mode, in air, in constant force regime.

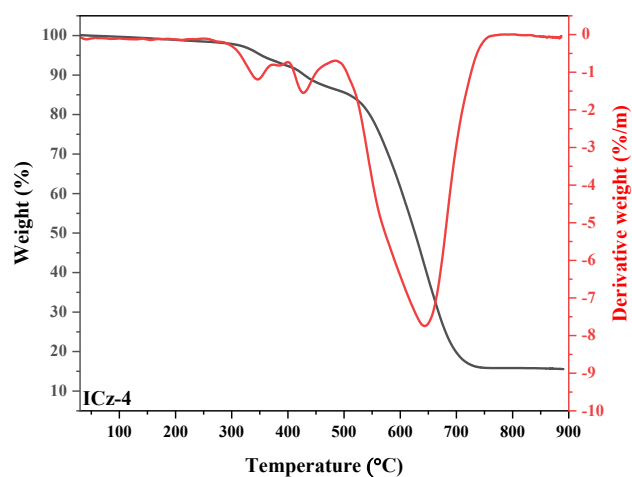
Multilayer OLEDs were prepared as follow:

All manipulations were made in a glove-box under an argon atmosphere. ITO-coated glass substrates with 12 Ohm/sq resistance (Lumtec, Taiwan) were cleaned by sequential ultrasonication in 15 % KOH aqueous solution, deionized water and 2-propanol for 15 minutes each, followed by drying with a dust-free nitrogen flow. The substrates were additionally treated by UV/ozone in UV-cleaning chamber (Ossila, UK) just prior use. A 40 nm-thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole-injective layer was first deposited. An aqueous solution of PEDOT:PSS (200 μl) was poured onto the preheated (70 °C) patterned ITO glass substrate, after which the substrate was rotated for 60 seconds at 2000 rpm. Finally, the deposited film was

annealed in Ar at 80 °C for 60 min. As a hole-transport and hole injection layer poly-TPD solution was spin-coated (2000 rpm) from chlorobenzene ($c = 5 \text{ gL}^{-1}$) and the layer was annealed in Ar at 100 °C. The emission layer was spin-coated from the solution on the resulted heterostructure. The ~30 nm-thick electron-transport/hole-blocking layer (TPBi) was thermally evaporated (Univex-300, Leybold-Heraeus) followed by a ~1 nm-thick LiF layer and a >100 nm-thick aluminum layer as the cathode under a pressure below 10^{-6} torr. The thickness of the layers was controlled by using of a quartz thickness monitor. EL spectra were recorded by Ocean Optics Maya Pro spectrometer, the volt-brightness and volt-current curves were measured using Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode.

Thermal measurements

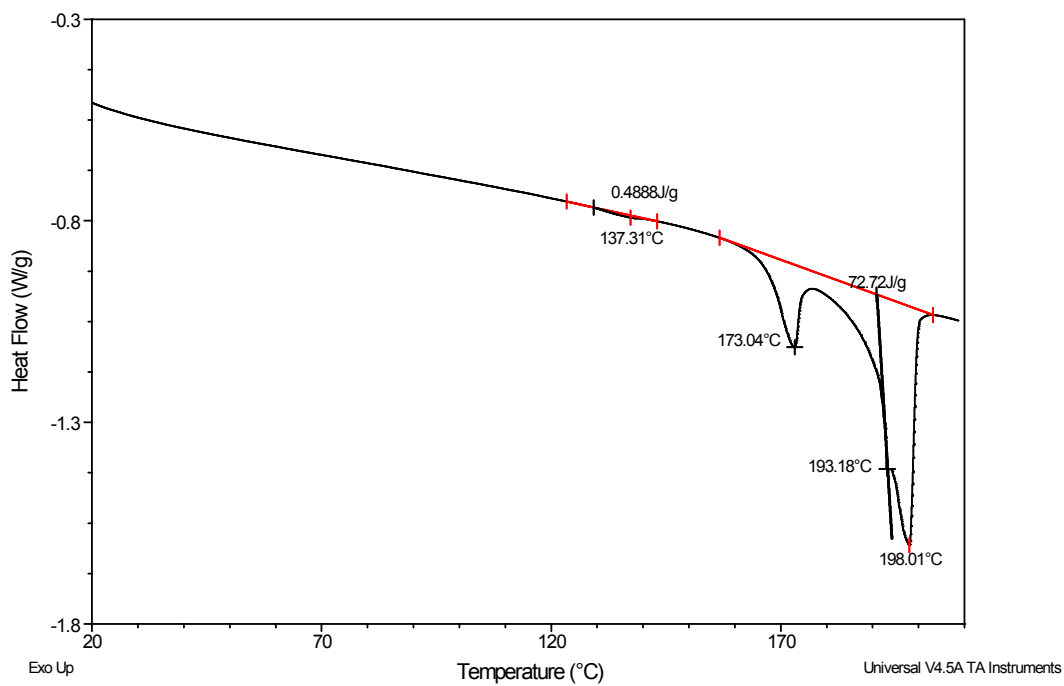




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Comment: ICB-3

DSC

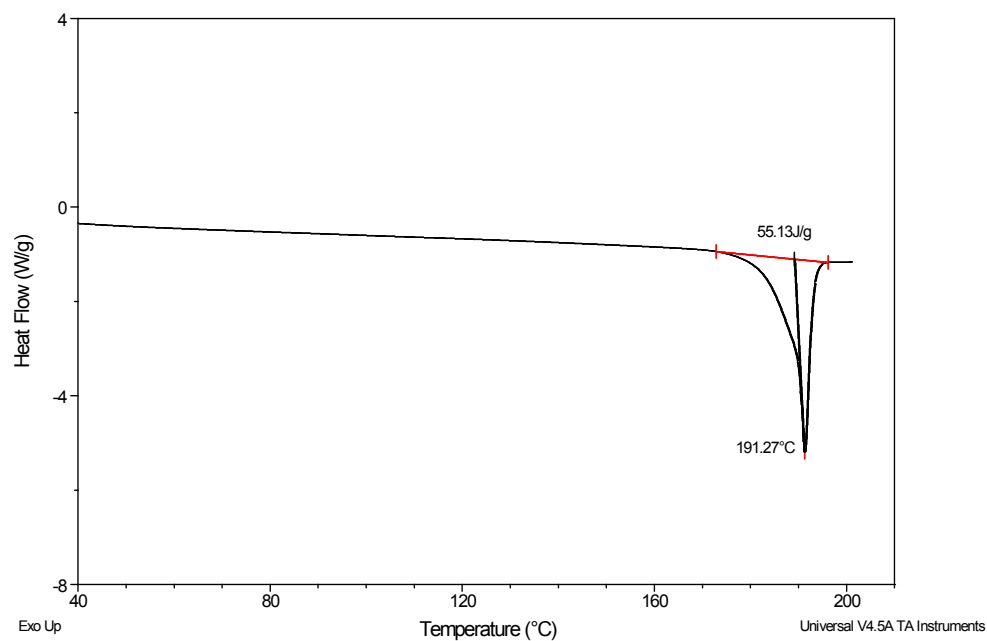
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Instrument: DSC Q2000 V24.11 Build 124



Sample: ICB4
Size: 1.3040 mg
Method: Ramp
Comment: 20 ICB4

DSC

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Instrument: DSC Q2000 V24.11 Build 124



Sample: ICz_1
Size: 9.8000 mg
Method: Ramp
Comment: ICz-1 mk=9.384

DSC

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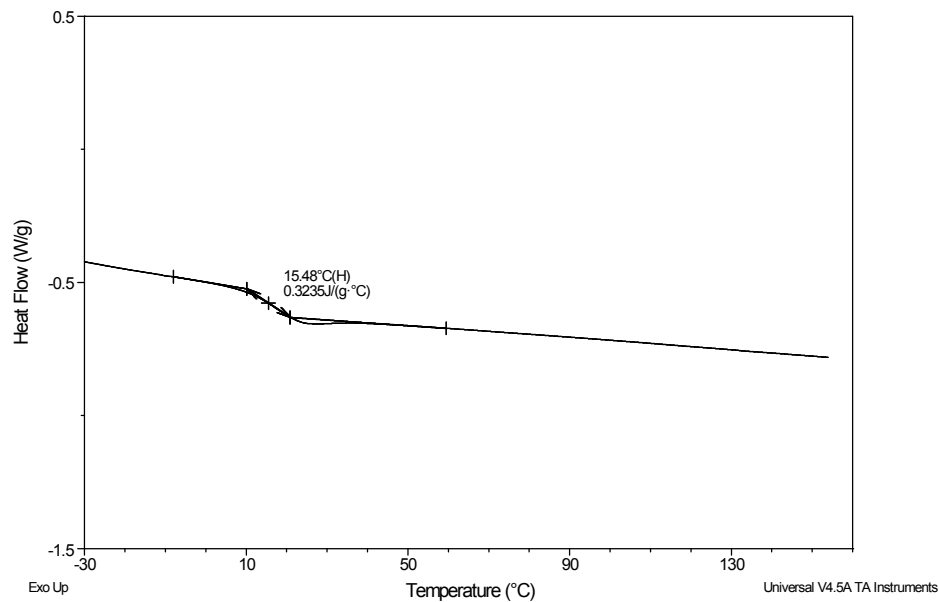


Fig. S1 Representative TGA, DTG and DSC curves.

Electrochemical and EPR measurements

Electrochemical and EPR measurements

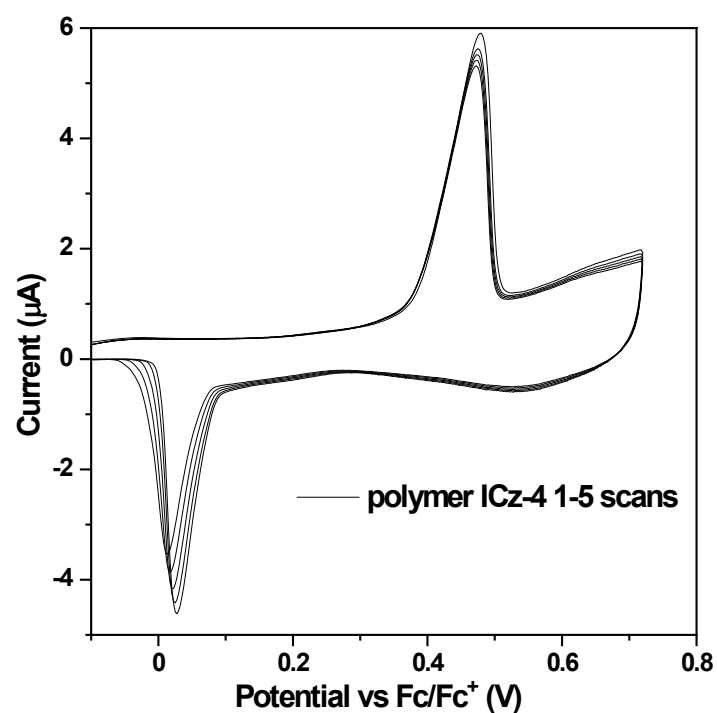


Fig. S2 CV curves of Polymer ICz-4 Polymer stay on the electrode surface. The measurements were performed with a platinum working electrode and referenced against Fc/Fc⁺ couple, scanning rate 50 mV/s in the electrolyte solution.

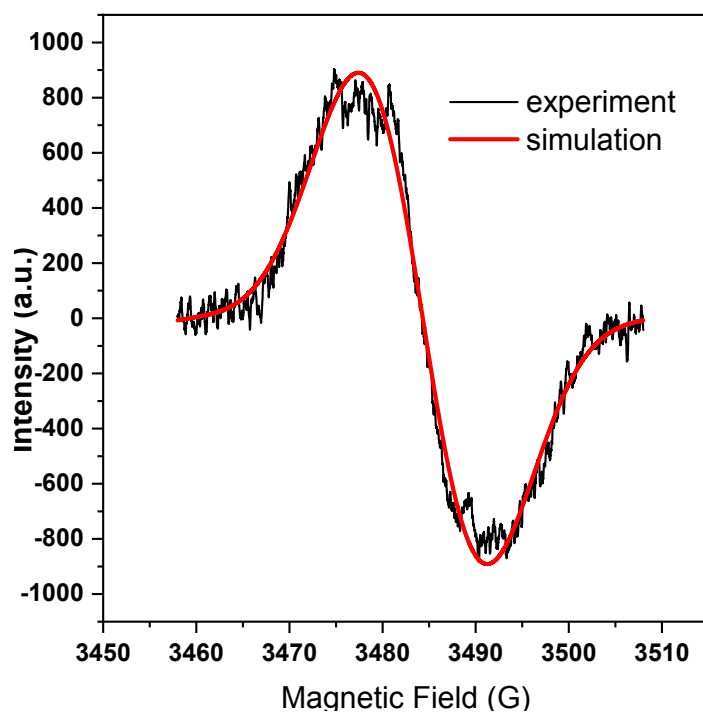


Fig. S3 EPR signal of radical cation of ICz-5 (black) and simulated curve (red).

Theoretical calculations

Table S1 TD-DFT calculated absorption and emission wavelength for **ICz-1** – **ICz-6**.

	Absorption [nm] (oscillator strengths)	Transitions	Emission [nm] (oscillator strengths) Transitions
ICz-1	370.12 (0.1080)	HOMO→LUMO (93%)	
	365.40 (1.8376)	HOMO→L+1 (98%)	
	305.88 (0.1700)	H-1→L+1 (90%)	
	279.82 (0.1885)	H-2→LUMO (62%), HOMO→L+4 (11%)	
	278.80 (0.1521)	H-2→L+1 (39%), HOMO→L+2 (38%), H-3→LUMO (18%)	438.91 (2.2278) HOMO→LUMO (99%)
	254.78 (0.1471)	H-7→LUMO (21%), H-2→L+2 (20%), HOMO→L+5 (18%), H-1→L+4 (11%),	396.01 (0.1434) HOMO→L+1 (96%)
	251.05 (0.1391)	H-1→L+2 (43%), H-6→LUMO (21%), H-5→LUMO (14%)	
	233.26 (0.3330)	H-7→L+1 (33%), H-2→L+4 (18%), H-3→L+2 (17%), H-2→L+3 (14%)	
ICz-2	344.88 (1.3120)	HOMO→L+1 (94%)	
	336.17 (0.5002)	HOMO→L+2 (88%)	
	286.92 (0.6176)	H-4→LUMO (30%), H-2→L+1 (26%), HOMO→L+4 (18%), H-1→L+2 (16%),	
	282.44 (0.1194)	HOMO→L+4 (70%), H-4→LUMO (12%)	423.85 (0.1275) HOMO→LUMO (97%)
	265.79 (0.1344)	H-2→L+2 (54%), HOMO→L+5 (22%)	372.07 (2.0265) HOMO→L+1 (98%)
	257.33 (0.1033)	H-4→L+3 (25%), H-6→LUMO (18%), H-1→L+4 (18%), H-2→L+4 (13%),	
	248.89 (0.2620)	H-1→L+3 (61%), H-5→LUMO (13%)	
	246.79 (0.3323)	HOMO→L+5 (42%), H-3→L+2 (24%)	
	241.04 (0.1589)	H-2→L+3 (47%), H-3→L+3 (22%), H-1→L+3 (16%)	
	372.28 (0.1144)	HOMO→LUMO (95%)	410.35 (0.1660) HOMO→LUMO (97%)
ICz-3	329.33 (1.5711)	HOMO→L+1 (98%)	
	287.90 (0.4207)	H-1→L+1 (49%), H-2→LUMO (41%)	358.49 (1.9122) HOMO→L+1 (98%)
	280.50 (0.1142)	HOMO→L+2 (63%), H-3→LUMO (32%)	

	272.24 (0.1109)	H-1→L+1 (47%), H-2→LUMO (39%)	
	246.82 (0.4854)	H-1→L+2 (74%)	
ICz-4	414.84 (1.6210)	HOMO→LUMO (99%)	519.18 (1.8552) HOMO→LUMO (99%)
	278.34 (0.2631)	H-3→L+1 (47%), HOMO→L+5 (34%)	
	277.76 (0.1155)	HOMO→L+5 (59%), H-3→L+1 (27%)	416.31 (0.1032) HOMO→L+1 (97%)
	254.09 (0.1529)	HOMO→L+7 (30%), H-6→LUMO (26%), HOMO→L+6 (12%)	
	252.81 (0.1113)	H-1→L+3 (43%), H-4→L+1 (25%)	
ICz-5	372.06 (1.0266)	HOMO→L+1 (95%)	449.15 (0.0500) HOMO→LUMO (98%)
	318.41 (0.5590)	HOMO→L+2 (45%), H-1→L+1 (39%)	
	316.42 (0.1334)	H-1→L+1 (50%), HOMO→L+2 (40%)	427.99 (0.9047) HOMO→L+1 (96%)
	289.97 (0.5024)	H-2→L+1 (61%), H-3→LUMO (22%)	
	278.76 (0.1016)	HOMO→L+6 (51%), HOMO→L+5 (18%), H-3→LUMO (13%)	
	275.80 (0.1751)	H-3→LUMO (51%), H-2→L+1 (32%)	
	255.71 (0.1386)	H-1→L+3 (76%), H-5→LUMO (14%)	
	243.65 (0.2969)	H-2→L+3 (72%)	
ICz-6	364.38 (0.1178)	HOMO→LUMO (93%)	CH ₂ Cl ₂ : 394.98 (0.1878) HOMO→LUMO (96%)
	339.71 (1.6668)	HOMO→L+1 (97%)	
	295.29 (0.2195)	H-1→L+1 (77%), H-3→LUMO (17%)	367.01 (2.0086) HOMO→L+1 (97%)
	279.74 (0.2201)	H-2→L+1 (50%), H-2→L+2 (21%)	
	276.50 (0.2426)	H-3→LUMO (61%), H-1→L+1 (15%), H-2→L+1 (12%)	In vacuum : S1 state: 395.08 (0.1625) HOMO→LUMO (96%)
	268.68 (0.1152)	H-1→L+2 (32%), H-4→L+1 (21%), HOMO→L+5 (18%), H-2→L+2 (11%), H-2→L+1 (10%),	
	255.64 (0.3479)	H-4→L+2 (37%), H-6→LUMO (12%), HOMO→L+5 (12%)	364.20 (1.9539) HOMO→L+1 (97%) 301.22 (0.346) H-2→LUMO (47%), H-1→L+1 (47%)
	244.83 (0.3329)	H-1→L+3 (57%), H-5→LUMO (22%), H-3→L+4 (15%)	S2 state: 387.58 (0.1452) HOMO→L+1 (95%) 399.29 (1.9843) HOMO→LUMO (98%)

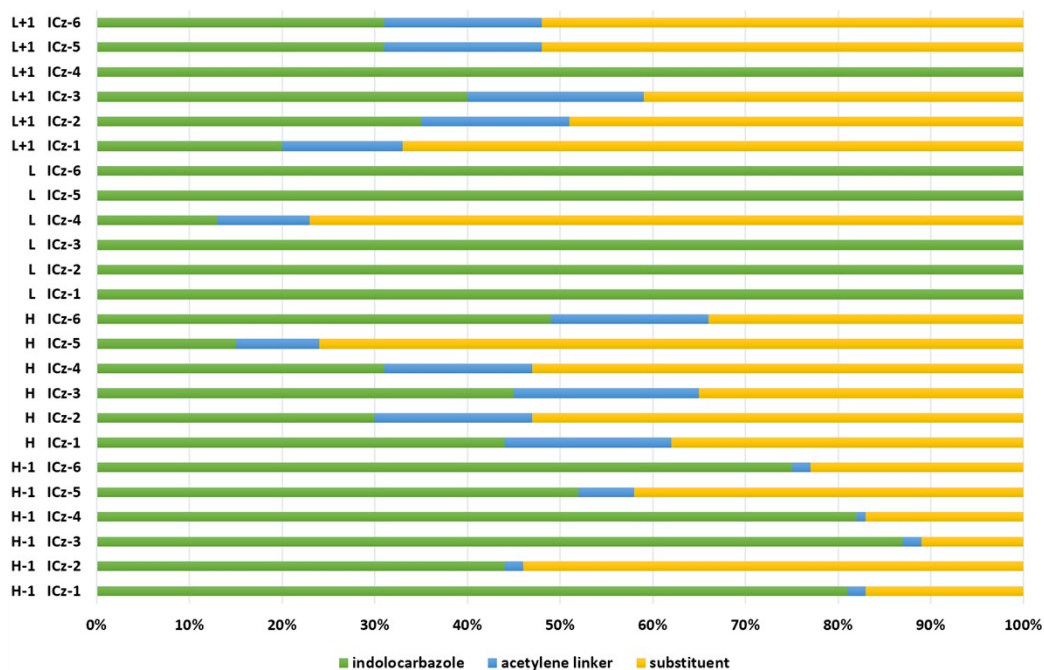


Fig. S4 Contribution of indolocarbazole/acetylene linker/substituent in the creation of orbitals H-1, H, L, L+1 for ICz-1 – ICz-6.

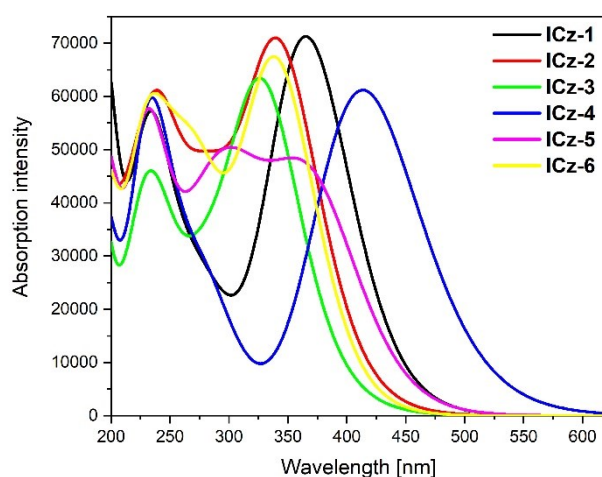


Fig. S5 TD-DFT calculated (6-31G(d,p)/B3LYP) absorption spectra in the dichloromethane solution of ICz-1 – ICz-6.

Table S2 Energies of HOMO and LUMO of ground state S_0 and singlet excited states S_1 , S_2 and calculated energy gap between S_1 and S_2 states.

	E_{HOMO} [eV]			E_{LUMO} [eV]			$\Delta E_{S_2-S_1}$ [cm^{-1}]
	S_0	S_1	S_2	S_0	S_1	S_2	
ICz-1	-5.26	-5.04	-	-1.45	-1.75	-	-
ICz-2	-5.07	-4.96	-4.96	-1.42	-1.59	-1.59	0.015
ICz-3	-5.23	-5.10	-5.00	-1.43	-1.59	-1.41	1894
ICz-4	-5.15	-4.88	-4.98	-1.78	-2.11	-1.94	3541
ICz-5	-5.04	-4.75	-4.66	-1.45	-1.64	-1.48	516
ICz-6	-5.35	-5.26	-5.14	-1.47	-1.62	-1.60	392

Optical measurements

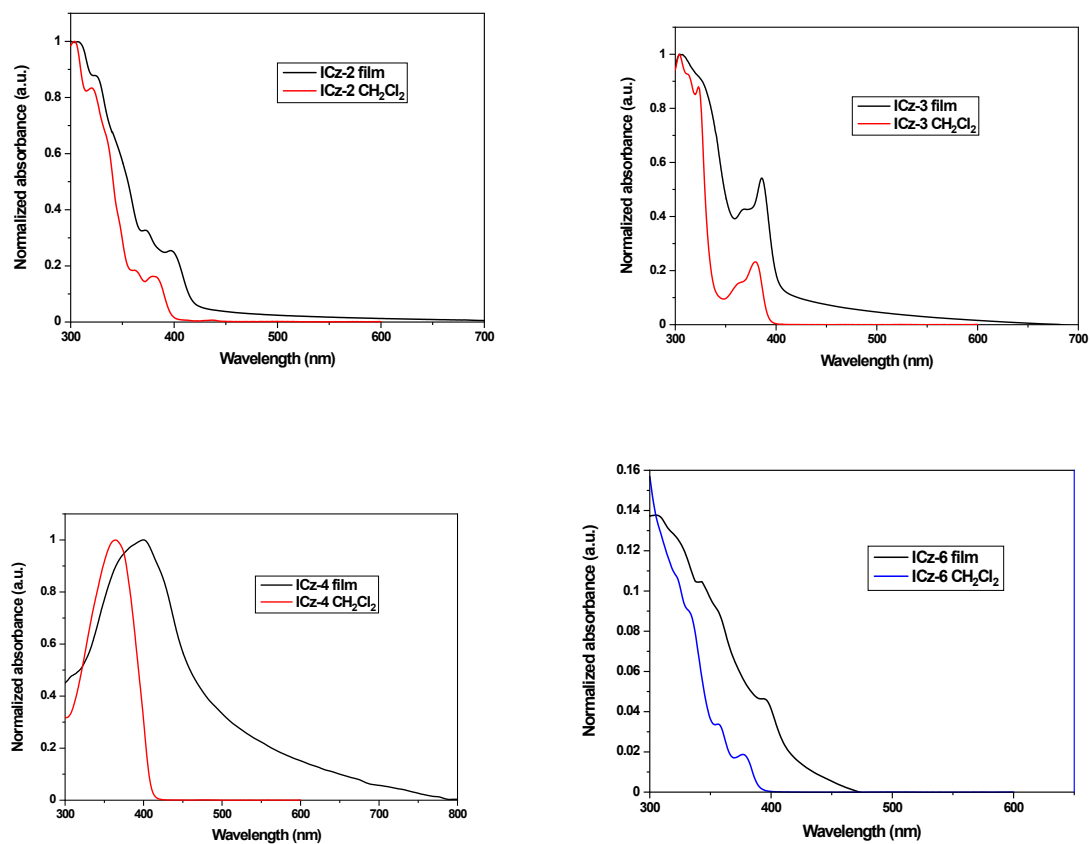


Fig. S6 The normalized absorption spectra of ICz-2 – ICz-4 and ICz-6 in solution and as thin solid films.

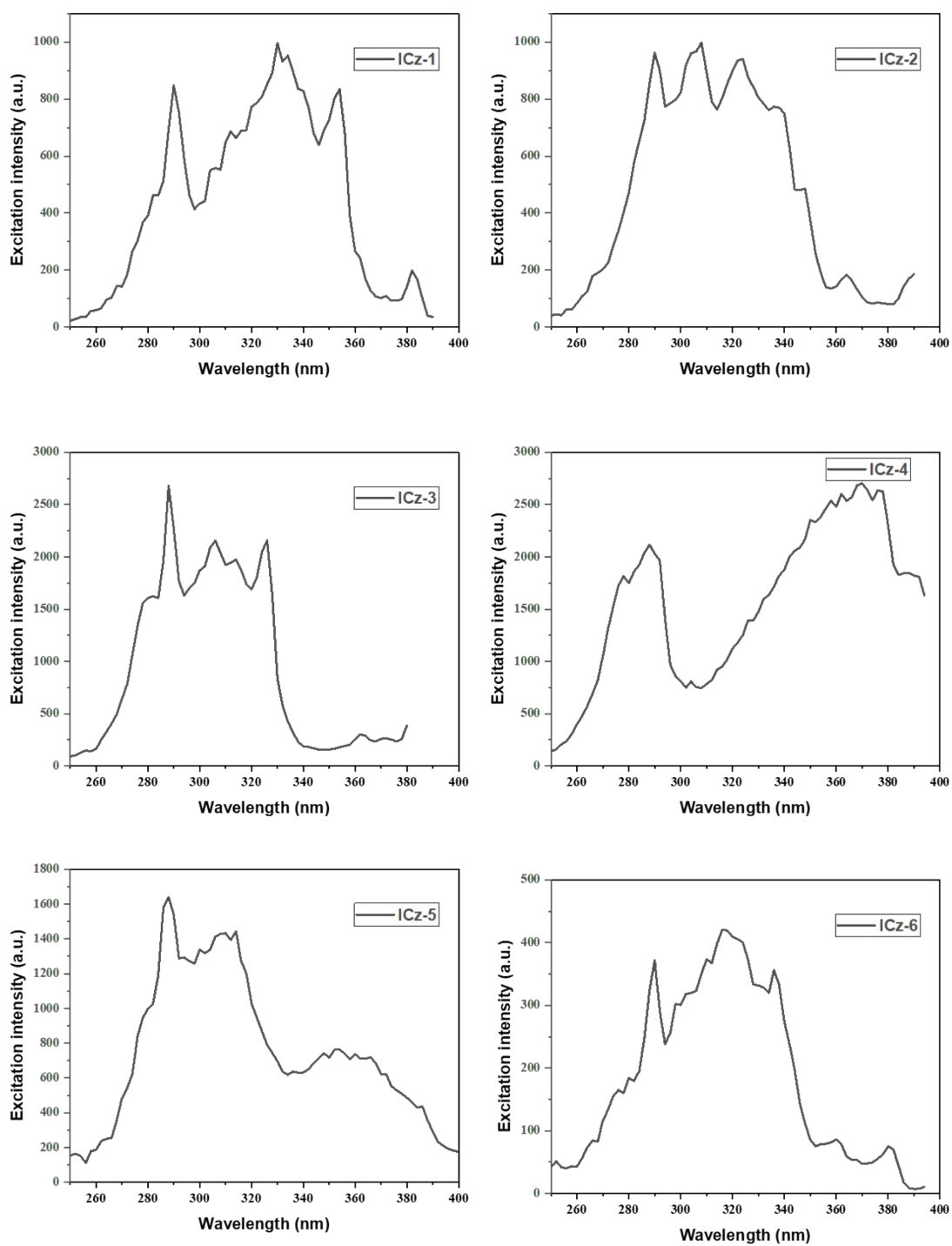


Fig. S7 Excitation spectra in ethanol:methanol 4:1 v/v solution at 77 K ($c = 10^{-5}$ mol/dm³).

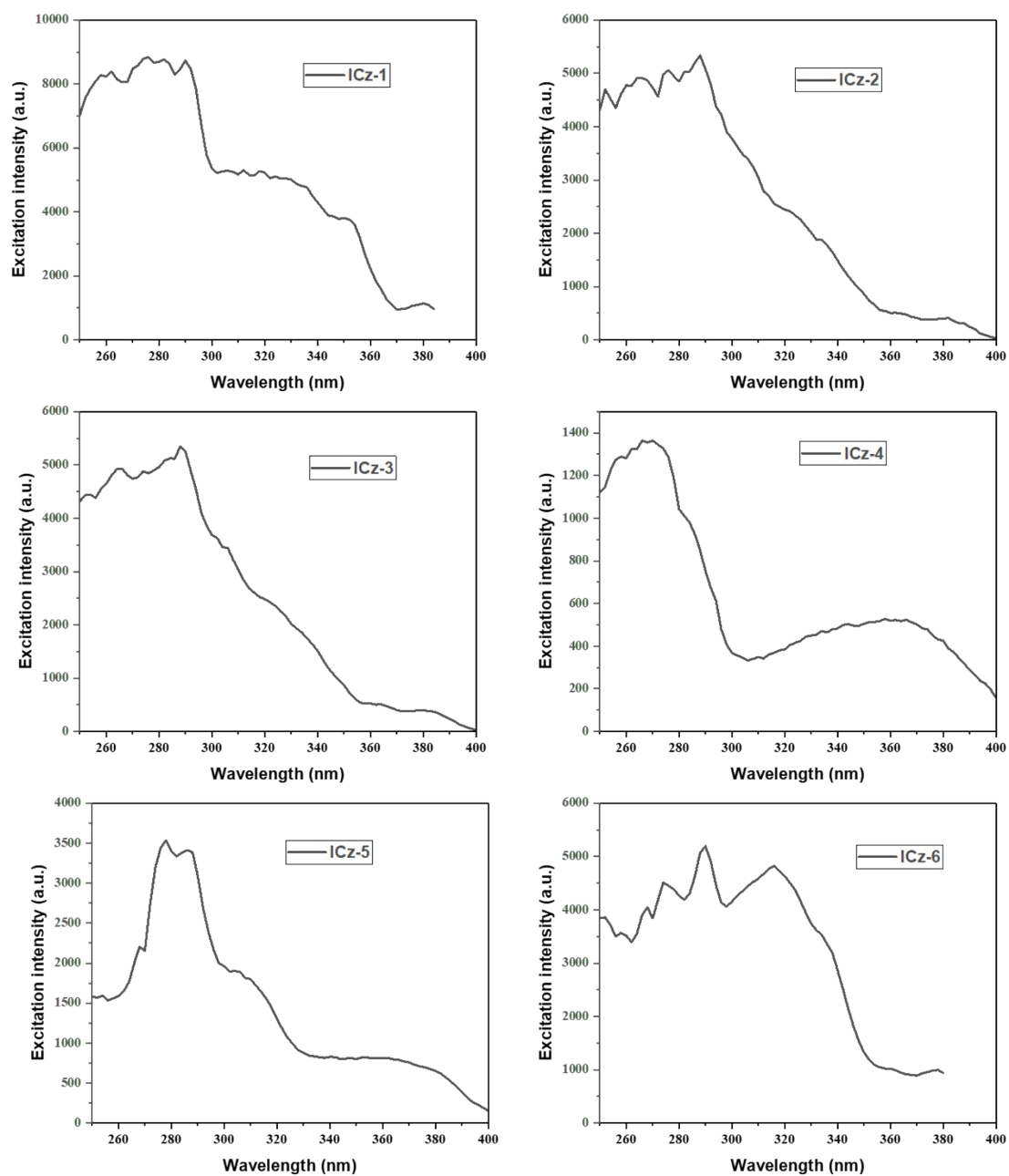


Fig. S8 Excitation spectra in dichloromethane solution at 298 K ($c = 10^{-5} \text{ mol/dm}^3$).

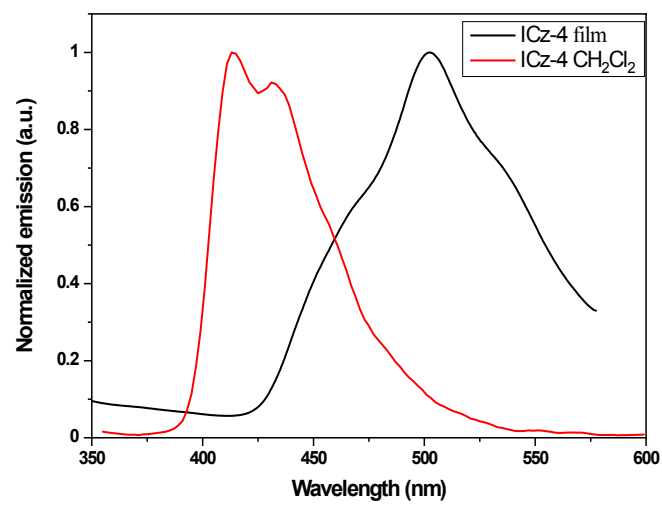
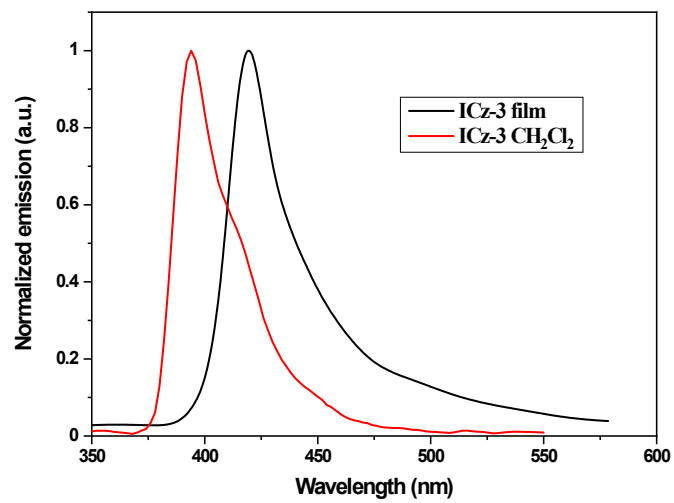
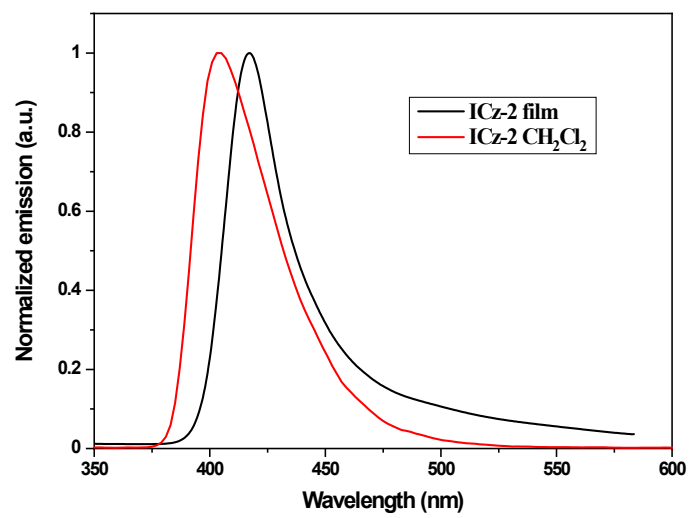
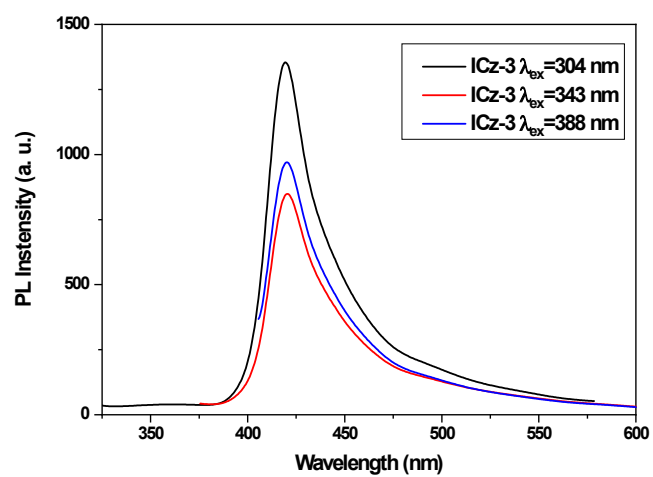
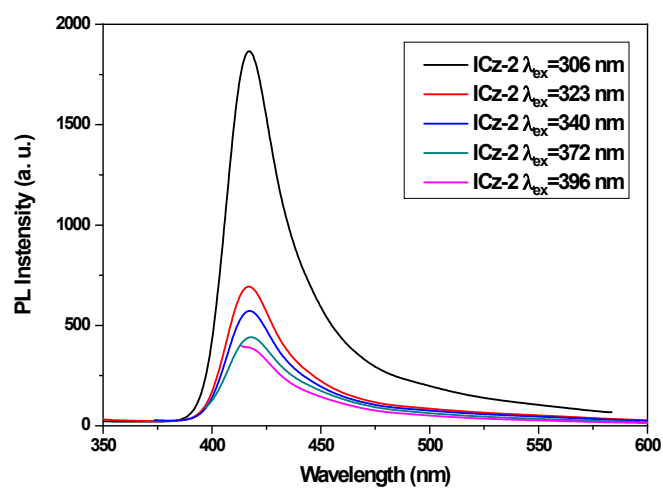


Fig. S9 The normalized PL spectra of ICz-2 – ICz-4 in solution and as thin solid films.



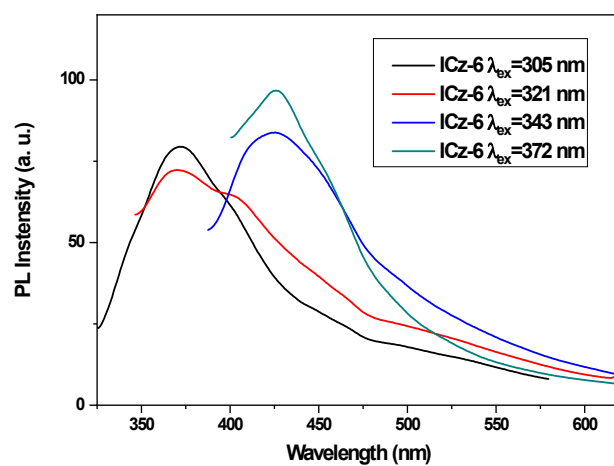
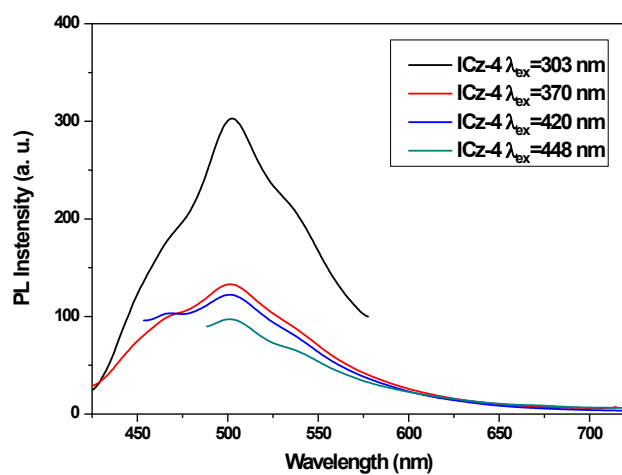
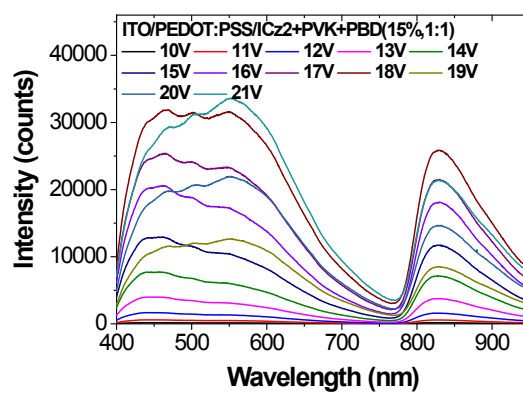
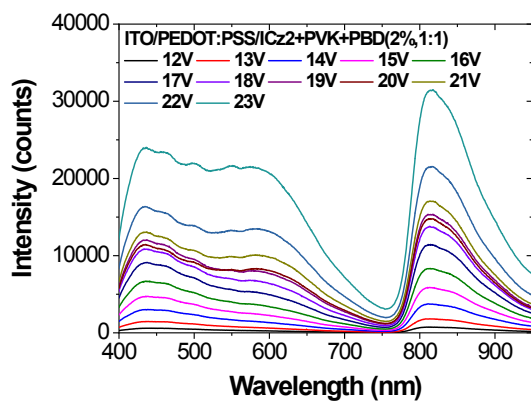


Fig. S10 PL spectra of the indolocarbazole derivatives in thin-film recorded under different excitation wavelength.

Electroluminescence measurements



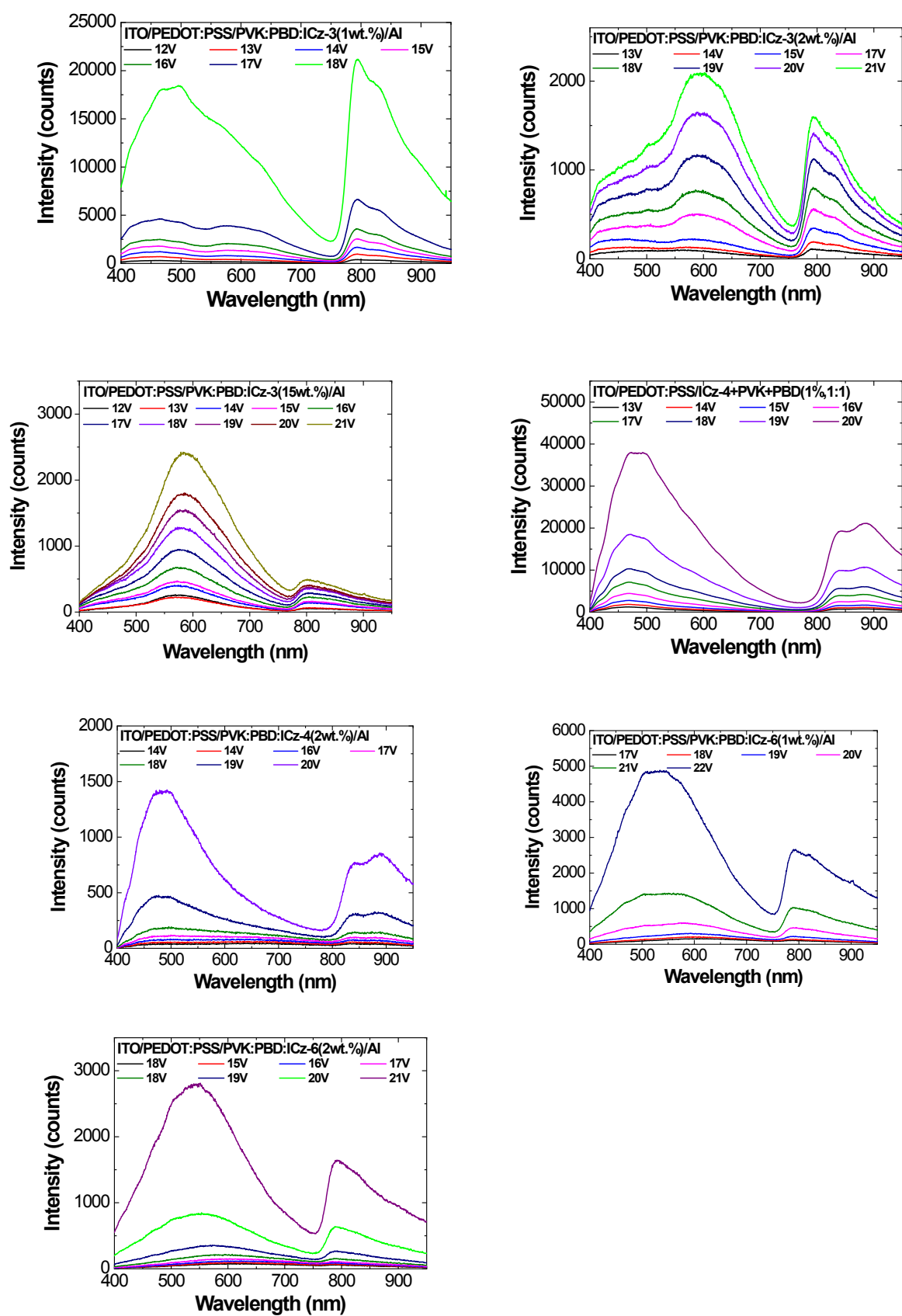


Fig. S11 EL spectra of fabricated diodes based on indolocarbazole derivatives.

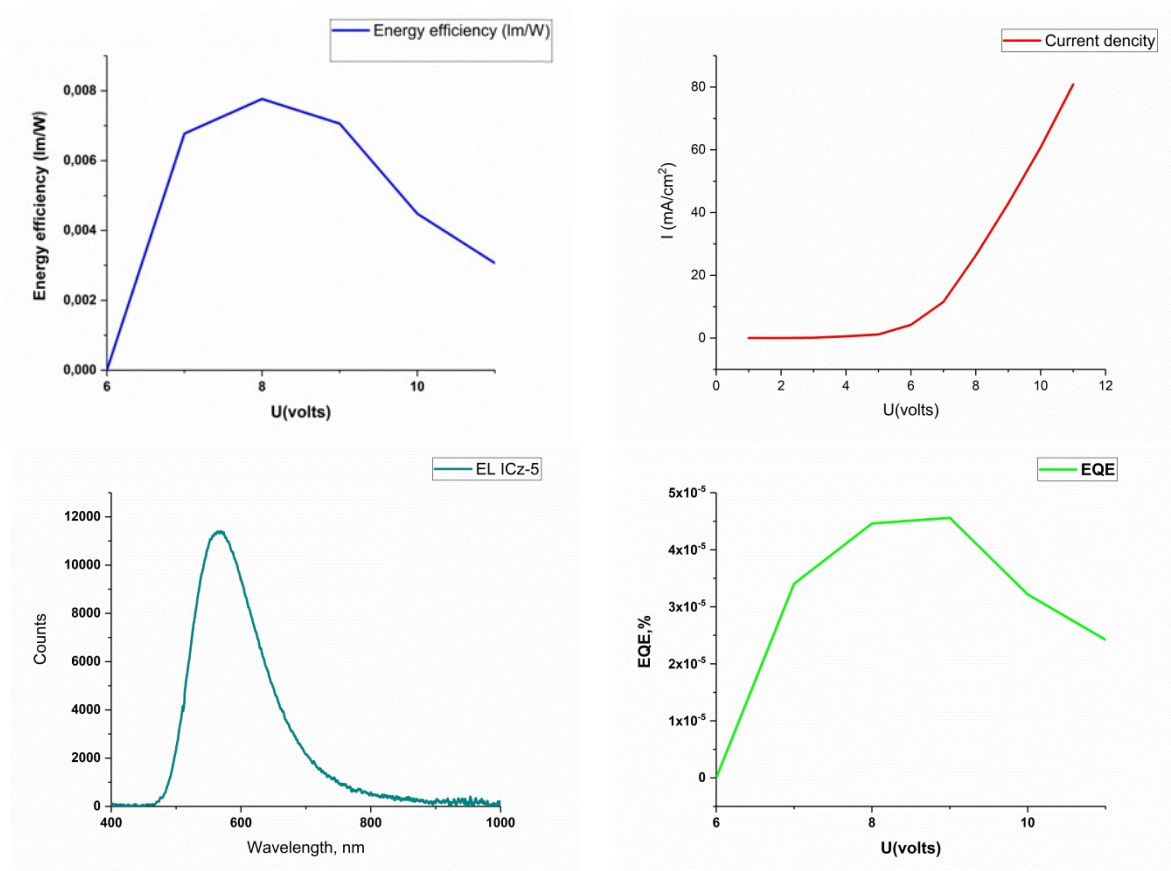


Fig. S12 Properties of multilayer OLED structures based on **ICz-5** compound.

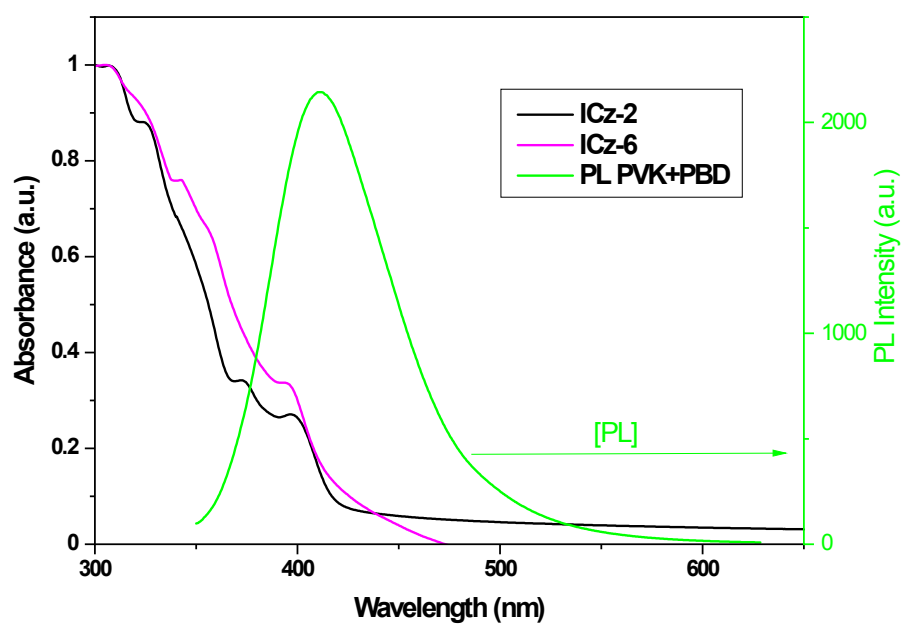


Fig. S13 Normalized UV-vis spectra of indolocarbazole derivatives in film and PL spectrum of PVK:PBD matrix.

NMR Spectra

