Supporting Information

Chemistry and Material based on 5,5'-bibenzo[c][1,2,5]thiadiazole

Supplementary Information[†]

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1. Synthesis and Characterization of the Compounds



Scheme S1. Synthesis of 4,4',7,7'-tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole core.

1,1'-bi(cyclohexa-1,5-diene)-3,3',4,4'-tetraamine (1)

A mixture of 1,1'-bi(cyclohexa-1,5-diene)-3,3',4,4'-tetraamine (6549 mg, 30 mmol) in 50 mL SOCl₂ with stirring while 2 mL of pyridine was added slowly. After completion of the pyridine addition, the reaction mixture was heated at 100 °C under reflux for 12 hs. The mixture was washed well with water then filtered, recrystallized from dichloromethane, and dried to give straw yellow power 6497.92 mg (80%). ¹H NMR (500 MHz, DMSO) δ 8.64 (S, 2H). 8.32-8.30 (d, 2H). 8.26-8.25 (d, 2H). FT-IR (KBr pellet, cm⁻¹): 410, 528, 587, 814, 850, 889, 904, 921, 1156, 1230, 1315, 1431, 1459, 1508, 1613, 1791, 3017, 3056, 3084. MALDI-TOF-MS: m/z = 271.2 (calcd. 270.33). Anal. Calcd for C₁₂H₆N₄S₂: C, 53.32; H, 2.24; N, 20.73; Found: C, 53.68; H, 2.13; N, 20.49.

4,4',7,7'-tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole (2)

A mixture of 5406.6 mg (20 mmol) of 5-chlorobenzo[c][1,2,5]thiadiazole in 50 mL of 45% hydrobromic acid was heated at 100 °C under reflux with stirring while 9.6 g (60 mmol,4.59 ml) of bromine was added slowly. After completion of the bromine addition, the reaction mixture was heated under reflux for another12 hs. The mixture was filtered, washed well with water,

recrystallized from dichloromethane, and dried to give straw yellow power 8202.86 mg (70%). ¹H NMR (500 MHz, DMSO) δ 8.18 (S, 2H). FT-IR (KBr pellet, cm⁻¹): 490, 505, 570, 585, 623, 660, 807, 839, 880, 910, 936, 1034, 1110, 1187, 1219, 1310, 1443, 1490, 1584, 2923, 3035. MALDI-TOF-MS: m/z = 585.3 (calcd. 585.92). ¹H NMR (500 MHz, CDCl₃): δ 7.73 (s, 2H). Anal. Calcd for C₁₂H₂Br₄N₄S₂: C, 24.60; H, 0.34; N, 9.56. Found: C, 24.53; H, 0.54; N, 9.37.



Scheme S2. Synthesis of benzo[1,2,5]thiadiazole derivative C1.

4,4',4'',4'''-(5,5'-bibenzo[c][1,2,5] thiadiazole-4,4',7,7'-tetrayl) tetrak is (N,N-diphenylaniline) (C1)

4,4',7,7'-tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole (585.92 mg, 1 mmol) and N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)aniline (1867.45 mg, 5 mmol) were dissolved in freshly distilled toulene (6 mL) under nitrogen. Potassium carbonate 2 M in water (4 mL) was added, together with ethanol (0.2 mL). The mixture was cooled in liquid nitrogen and thoroughly degassed. And them tetrakis(triphenylphosphine) palladium(0) (103.95 mg) was added and the resulting mixture was vigorously stirred at 80 °C for 60 hs. After cooling to room temperature, dichloromethane was added and the water phase was extracted. The organic phase was collected and dried with anhydrous magnesium sulphate. After evaporation of the solvent, the residue was purified via chromatography by petroleum ether: dichloromethane = 1: 2. The desired compound was obtained in 60% yield (746.12 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.70-7.68 (d, 4H),7.62 (s, 2H), 7.37-7.35 (d, 4H), 7.32-7.28 (t, 8H), 7.20-7.18 (d,12H), 7.14-7.09 (m,12H), 7.06-7.04 (d,8H), 6.99-6.98 (m,8H). ¹³C NMR (125 MHz, CDCl₃) 121.88, 122.71, 123.41, 125.03, 129.31, 129.41, 129.80, 130.42, 131.16, 131.20, 131.84, 132.22, 139.20, 147.25, 147.42, 147.56, 148.17, 153.09, 155.90. FT-IR (KBr pellet, cm⁻¹): 509, 524, 614, 696, 754, 840, 887, 1030, 1077, 1182, 1205, 1275, 1329, 1485, 1516, 1594, 3035, 3058. MALDI-TOF-MS: m/z = 1243.9 (calcd. 1243.54). Anal. Calcd. for C₈₄H₅₈N₈S₂: C, 81.13; H, 4.70; N, 9.01. Found: C, 81.34; H, 4.60; N, 9.25.



Scheme S3. Synthesis of benzo[1,2,5]thiadiazole derivatives L2 and C2.

4,4',4'',4'''-(5,5',5'',5'''-(5,5'-bibenzo[c][1,2,5]thiadiazole-4,4',7,7'-tetrayl)tetrakis(thiophene-5,2 -diyl))tetrakis(N,N-diphenylaniline) (C2)

A mixture of 4,4',7,7'-tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole (585.92 mg, 1 mmol) and N,N-diphenyl-4-(5-(tributylstannyl)thiophen-2-yl)aniline (3698.94, 6 mmol) in toluene (50 mL) was carefully degassed before and after Pd[PPh₃]₄ (103.95 mg) was added. The mixture was heated at 110 °C, stirred under nitrogen for 30 hs, and then allowed to cool to room temperature. The mixture was poured into a large amount of methanol, and the resulting precipitate was collected by filtration afford the compounds as dark solids. The mixture was purified on silica gel eluting with dichloromethane to afford the products as dark solids 471.61mg (30%). ¹H NMR (500 MHz, CDCl₃): δ 8.02-8.01 (d, 2H), 7.83 (s, 2H), 7.50-7.48 (d, 4H), 7.34-7.33 (m, 6H), 7.27-7.23 (m, 12H), 7.22-7.20 (d, 6H), 7.12-7.10 (d, 8H), 7.06-6.99 (d, 22H), 6.97-6.95(d, 4H). ¹³C NMR

(125 MHz, CDCl₃) 122.79, 123.65, 123.72, 123.81, 124.97, 125.05, 125.31, 126.39, 127.04, 127.10, 128.32, 129.44, 129.74, 132.10, 135.46, 137.63, 139.73, 146.42, 147.51, 147.77, 148.07, 152.34, 155.34. FT-IR (KBr pellet, cm⁻¹): 515, 624, 697, 749, 806, 836, 888, 1035, 1070, 1109, 1173, 1191, 1273, 1321, 1455, 1490, 1537, 1594, 3029, 3056. MALDI-TOF-MS: m/z = 1572.2 (calcd. 1572.04). Anal. Calcd. for $C_{100}H_{66}N_8S_6$: C, 76.40; H, 4.23; N, 7.13. Found: C, 76.15; H, 4.14; N, 7.12.



Scheme S4. Synthesis of benzo[1,2,5]thiadiazole derivative C3.

4,7-dibromo-5-chlorobenzo[c][1,2,5]thiadiazole (1)

A mixture of 3.41g (20 mmol) of 5-chlorobenzo[c][1,2,5]thiadiazole in 50 mL of 45% hydrobromic acid was heated at 100 °C under reflux with stirring while 9.6 g (60mmol,4.59mL) of bromine was added slowly. After completion of the bromine addition, the reaction mixture was heated under reflux for another 12 hs. The mixture was filtered, washed well with water,

recrystallized from acetone, and dried to give straw yellow power 4.60g (70%). ¹H NMR (500 MHz, CDCl₃): δ 8.36 (s,1H). MALDI-TOF-MS: m/z = 328.6 (calcd. 328.41). Anal. Calcd for C₆HBr₂ClN₂S: C, 21.94; H, 0.31; N, 8.53. Found: C, 21.81; H, 0.33; N, 8.36.

4,4'-(1E,1'E)-2,2'-(5-chlorobenzo[c][1,2,5]thiadiazole-4,7-diyl) bis (ethene-2,1-diyl) bis (N,N-dipharka) bis (N,N-dipharka)

enylaniline) (A)

(0.66g, 2.00 mmol) and N,N-diphenyl-4-vinylaniline (1.09 g, 4.00 mmol), Pd(OAc)₂ (26.94 mg, 0.12 mmol), K₃PO₄ (1.27 g, 6.00 mmol) were dissolved in 20 mL degassed and freshly distilled DMAC in a 50 mL over-dried flask equipped with a magnetic stirring bar and connected with condenser. Then the reaction mixture was heated to100 °C under nitrogen atmosphere and kept 24 hs. Then 20 mL water was poured into the solution to stop the reaction. The violet precipitate was filtered off and washed with water. The solid was dissolved in methylene chloride and dried over MgSO₄. The resulting compound was precipitated twice from methanol and further purified by column chromatography (silica gel, dichloromethane : petroleum ether = 1 : 4, Rf: 0.32) to obtain a red solid 0.74 g (yield: 52%). ¹H NMR (500 MHz, CDCl₃): δ 8.514-8.482 (d,1H), 7.914-7.881 (d,1H) , 7.684 (s, 1H), 7.631-7.599 (d, 1H), 7.560-7.543 (d, 2H), 7515-7.498 (d, 2H), 7.471-7.439 (d, 1H), 7.300-7.269 (m, 8H), 7.151-7.134 (d, 8H), 7.098-7.046 (m, 8H). FT-IR (KBr pellet, cm⁻¹): 502, 620, 704, 755, 822, 915, 966, 1028, 1075, 1172, 286, 1328, 1492, 1513, 1589, 2854, 2919, 3036, 3059. MALDI-TOF-MS: m/z = 708.6 (calcd. 709.30). Calcd for C₄₀H₃₃CIN₄S: C, 77.89; H, 4.69; N, 7.90. Found: C, 77.75; H, 4.56; N, 7.70.

4,4'-(1E,1'E)-2,2'-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole-4,7 -diyl)bis(ethene-2,1-diyl)bis(N,N-diphenylaniline) (B)

A solution of (A) (0.71 g, 1.00 mmol), 4, 4, 4', 4', 5, 5, 5', 5' -octamethyl- 2, 2' - bi (1, 3, 2

-dioxaborolane)(0.30 g, 1.20 mmol), Pd(dppf)Cl₂ (0.04 g, 0.05 mmol), and KOAc(0.59 g, 6.00 mmol) in degassed 1,4-dioxane (5 mL) was stirred at 90 °C under nitrogen atmosphere for 2 days. The reaction was quenched by adding water, and the resulting mixture was washed with dichloromethane. The organic layers were collected, dried over MgSO₄, and concentrated in vacuum. It was then purified via silica gel chromatography by petroleum ether: dichloromethane = 3:2 to give the desired compound as a red solid 0.40 yield (50%). ¹H NMR (500 MHz, CDCl₃): δ 8.49-8.46 (d,1H), 8.26-8.23 (d,1H) \neq 8.00 (s, 1H),8.01-7.98 (d, 1H), 7.55-7.49 (m, 5H), 7.30-7.27 (m, 8H), 7.15-7.13(m, 8H), 7.10-7.03 (m, 8H). FT-IR (KBr pellet, cm⁻¹): 503, 617, 642, 688, 756, 819, 857, 966, 1147, 1173, 1282, 1333, 1447, 1493, 1506, 1586, 2850, 2927, 3034, 3053. MALDI-TOF-MS: m/z = 802.1 (calcd. 803.2). Anal. Calcd for C₅₂H₄₅BN₄O₂S: C, 77.99; H, 5.66; N, 7.00. Found: C, 77.71; H, 95; N, 7.26.

4,4',4'',4'''-(1E,1'E,1''E,1''E)-2,2',2'',2'''-(5,5'-bibenzo[c][1,2,5]thiadiazole-4,4',7,7'-tetrayl)tetr akis(ethene-2,1-diyl)tetrakis(N,N-diphenylaniline) (C3)

(A)(0.14 g, 0.2 mmol) and (B) (0.16 g, 0.2 mmol) were dissolved in freshly distilled toulene (3 mL) under nitrogen. Potassium carbonate 2 M in water (2 mL) was added, together with ethanol (0.2 mL). The mixture was cooled in liquid nitrogen and thoroughly degassed. And then tetrakis(triphenylphosphine) palladium(0) (18.0 mg) was added and the resulting mixture was vigorously stirred at 80 °C for 60 hs. After cooling to room temperature, dichloromethane was added and the water phase was extracted. The organic phase was collected and dried with anhydrous magnesium sulphate. After evaporation of the solvent, the residue was purified via chromatography by petroleum ether: dichloromethane = 1: 2. The desired compound was obtained

in 72% yield (194.00 mg). ¹H NMR (500 MHz, CDCl₃): δ 8.45-8.42 (d, 2H),7.93-7.90 (d, 2H), 7.61 (s, 2H), 7.55-7.51 (d, 2H), 7.48-7.46 (d,4H), 7.28-7.25 (t,8H), 7.22-7.18 (m,12H), 7.12-7.11 (d,8H), 7.06-6.98 (m,22H), 6.91-6.90 (d,4H). ¹³C NMR (125 MHz, CDCl3) 121.85, 122.31, 122.95, 123.12, 123.22, 123.32, 12.73, 124.81, 126.86, 127.85, 127.89, 128.76, 129.27, 129.35, 129.72, 131.36, 131.94, 133.22, 136.13, 139.78, 147.39, 147.45, 147.87, 148.04, 154.04, 154.25. FT-IR (KBr pellet, cm⁻¹): 502, 614, 695, 755, 816, 856, 901, 965, 1033, 1077, 1174, 1276, 1330, 1489, 1509, 1587, 3034, 3057. MALDI-TOF-MS: m/z = 1347.2 (calcd. 1347.69). Anal. Calcd. for C₉₂H₆₆N₈S₂: C, 81.99; H, 4.94; N, 8.31. Found: C, 81.71; H, 4.87; N, 8.13.

2. Summary of the solubility and absorption coefficients (ϵ_{max}) of the linear and cruciform molecules.

Table S1 the performance of the solubility and the solution absorption coefficients (ε_{max}) of the linear and cruciform molecules.

Compounds	Solubility [mg mL ⁻¹]	T _g [°C]	$\mathbf{E}_{max} [M^{-1} cm^{-1}]$
L1	9.0	87	461(23764)
C1	12.0	181	472(40964)
L2	1.8	114	530(36547)
C2	2.5	171	527(70597)
L3	7.0	102	512(33586)
C3	10.0	112	539(58500)

3. Molecular simulation (the ground state).



Figure S1. The sketch maps of 3D structure of L1, C1, L2 and C2 at the ground state by molecular simulation.

Generally, with the chain length of non-substituted oligophenyls increasing their solubility decreases dramatically, however, the cruciform molecule displays higher solubility than that linear ones. The higher solubility should be contributed to the non-planar fragments of the cruciform molecules. The quantum-chemical simulations (Figure S1) indicate that in their most stable conformations, the molecules of C2 and C3 are cruciform and centrally symmetrical molecules in which there are dihedral angles of the BBTz core. So that the twist structures of molecules endow

them better solubility relative to the linear ones.

4. The thermal properties of linear (L1-L3) and cruciform molecules.





Figure S2. Differential scanning calorimetry (DSC) (a, c and e) and thermogravimetric analysis (TGA) (b, d and f) measurement of linear molecules and cruciform molecules.

Figure.S2 is the TGA and DSC spectra of the eight compounds. From DSC we can see that most of the linear molecules have tendency to crystalline. The cruciform ones do not show any thermodynamic processes in the scanning cycles, besides endothermic step-transition which can be attributed to the T_g . This suggests that the material could form homogeneous and amorphous films, which can avoid the problems associated with the presence of grain boundaries in polycrystalline films. Specifically, no crystallization or phase transition is observed for the cruciform ones upon heating beyond T_g . As can be seen that the eight materials are thermally stable with 5% weight loss up to 382-543 °C under nitrogen, indicating of good thermal stability.

5. Calculated energy profile of BBTz and C3 for rotation about the BBTz bond. (Dash line: thermal energy kT at room temperature (25 meV)).



Figure S3. Calculated energy profile of BBTz and C3 for rotation about the BBTz bond. (Dash line: thermal energy kT at room temperature (25 meV))

The total energy of BBTz and C3 was calculated by using density functional theory (DFT) at the B3LYP/6-31G level as implemented in Gaussian 03 for different conformations with fixed dihedral angles. The energy was plotted against the dihedral angle of the BBTz unit from 30 to 150°. The quantum-chemical simulations indicate that in its most stable conformation, C3 is a cruciform and centrally symmetrical molecule in which there is a 75° dihedral angle between one meta-positioned arm and one ortho-positioned arm. Upon rotation about the BBTz bond, a series of conformations indicate that a wide range of approximately 58 to 113 are close in energy. The energy barrier between 58 and 113 are slightly higher than the thermal energy kTat room temperature (25 meV). Therefore, theoretically,

mild conditions can trigger free rotation about the aryl-aryl bond in C3 to give a series of different conformations. The quantum-chemical simulations indicate that BBTz bond is rigide, there is a high energy barrier between two stable conformation.



6. The photophysical properties



Figure S4. Photoluminescence spectra of linear molecules (a: L1, c: L2 and e: L3) and cruciform

molecules (b: C1, d: C2 and f: C3) in different solvents.



Figure S5. Normalized UV-Vis absorption spectra of small molecules (a) L1, C1, (b) L2, C2, (c) L3, C3 in dilute chloroform solution and thin films at room temperature.

The photophysical properties of these linear molecule and cruciform in dilute chloroform solution (concentration 10^{-5} M) were studied and the main optical properties are listed in Table S2. All of these benzothiadiazole-based materials showed red emission in solution. Figure S4 shows the photoluminescence (PL) spectra of these materials red shift, which the solution polar increasing, indicating that the intramolecular charge transfer (ICT) transition between around substitute moiety and benzothiadiazole (BT) unit. The strong charge-transfer character of the molecule will affect the spectra red- shift can efficiently make red emission materials, also extend the absorption spectrum of the molecule for better matching the solar spectrum. As can be seen, all these benzothiadiazole-based materials display red emission with the $\lambda_{max, PL}$ in dilute toluene of L1 is 571 nm, L2 is 628 nm and L3 is 600 nm, 566 nm for C1, 648 nm for C2 and 631 nm for C3, respectively. The PL_{max} of the cruciform materials display red shift relative to the linear materials except the C1, which has a strong intramolecular twist. Figure S5 shows that the strong charge-transfer character of the moleculeC1, C2, C3, L1, L2 and L3 can efficiently extend the absorption spectrum of the molecule for better matching the solar spectrum. The relatively absorption coefficients (ε_{max}) could be calculated from Beer's law equation with the same dilute concentration of the linear and cruciform compounds in chloroform solution. The ε_{max} of L1 is 23764 (461 nm), C1 is 40964 (472 nm); L2 is 36547 (530 nm), C2 is 70597 (528 nm); L3 is 33586 (512 nm), C3 is 58500 (541 nm). The cruciform ones have higher ε_{max} than the linear ones because there are more dyeing unites.

	In toulene sol	In toulene solution		In film			
Compounds —	λ^{abs}_{max} [nm]	$\lambda^{PL}_{max}{}^{[nm]}$	λ^{abs}_{max} [nm]	λ^{PL}_{max} [nm]	HOMO [eV]	LUMO [eV]	ΔEg [eV]
L1	314,461	573	316,471	599	-5.18	-3.10	2.08
C1	315,472	566	313,480	587	-5.23	-3.20	2.03
L2	306,370,530	628	315,379,542	666	-5.22	-3.35	1.87
C2	305,361,527	648	308,364,539	657	-5.04	-3.33	1.71
L3	307,376,512	600	303,372,514	647	-5.24	-3.16	2.08
C3	305,365,539	631	310,373,540	667	-5.14	-3.23	1.91

Table S2. The optical and electrochemical of the linear (L1, L2, L3) and cruciform (C1, C2, C3) molecules.

7. The electrochemical properties

In order to determine the HOMO and LUMO energy levels of the oligomers, electrochemical cyclic voltammetry (CV) was carried out. TBAPF₆ was used as supporting electrolyte in acetonitrile solution with platinum button working electrodes, a platinum wire counterelectrode, and an Ag/AgNO₃ reference electrode under the N₂ atmosphere. Ferrocene was used as the internal standard. The redox potential of Fc/Fc+ which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration is located at 0.08 V in 0.1 MTBAPF6/acetonitrile solution. (LYW) HOMO and LUMO energy levels as well as the energy gap were calculated according to the following equations:

HOMO(eV) = - $|4.8 + \text{Eox} - (\phi \text{pa-Fc} + \phi \text{pc-Fc})/2|$ LUMO(eV) = - $|4.8 + \text{E}_{\text{red}} - (\phi_{\text{pa-Fc}} + \phi_{\text{pc-Fc}})/2|$. $E_g^{\text{ec}}(\text{eV}) = e(E_{\text{ox}}^{\text{onset}} - E_{\text{red}}^{\text{onset}})$ where Eoxonset and Eredonset are the measured onset potentials relative to Ag/Ag+. The results of the electrochemical measurements and calculated energy levels of the small molecules are listed in Table S3.

Table S3. Electrochemical data of the linear (L1, L2, L3) and cruciform molecules

$(\mathbf{C}1$	C^{2}	(C2)
(UI,	C2,	C3).

Complex	E _{onset} ^{ox} [V]	E _{onset} ^{red} [V]	HOMO [eV]	LOMO [eV]	$\Delta E_g [Ev]$
L1	0.59	-1.63	-5.18	-3.10	2.08
C1	0.64	-1.53	-5.23	-3.20	2.03
L2	0.63	-1.40	-5.22	-3.35	1.87
C2	0.44	-1.40	-5.04	-3.33	1.71
L3	0.52	-1.56	-5.24	-3.16	2.08
C3	0.41	-1.50	-5.14	-3.23	1.91

8. Theoretical simulation (density functional theory, B3LYP/6-31G)

Based on the results of theoretical simulation (density functional theory, B3LYP/6-31G),11 the geometry and electronic properties of these oligomers have been further revealed. The simulated electronic structure of complexes are given (Figure S6), the geometry, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are presented. The HOMO are almost extended across the whole molecular fragment and the LUMO are mainly on the benzothiadiazole unites. The exciton dissociation and decrease their recombination with charged species in peripheral conjugated sites. Such natural properties of charge carrier separation in benzothiadiazole unites meet the requirement of photovoltaic cell applications.





Figure. S6: Molecular orbital surfaces of the HOMO and LUMO obtained at B3 LYP/6-31G* level for the linear and cruciform molecules.

9. Electroluminescent properties

The solution process makes many potential mass-manufactural technologies possible, such as the inkjet printing and screen printing technologies. Herein we will investgate the properties of the spin-coating electroluminesence (EL) device based on C1 and L1. The EL properties of C1 was tested by utilizing it as an emissive layer with the structure of the OLED is indium tin oxide ITO/PEDOT:PSS (40 nm)/PVK (40 nm)/C1 (~60 nm) /CsF (0.5 nm)/Al (100 nm). The the device of C1 emits a red light ($\lambda_{max,EL} = 610$ nm) and its CIE coordinates are (0.59,0.41) (Table S4.). The turn-on voltage, maximum power efficiency and maximum luminance before damaged are 4.0 V, 0.67 lm W⁻¹ and 761 cd m⁻²,

respectively. For comparison, a similar device with L1 as the emission layer is also prepared under the same conditions. Its EL spectrum shows a maximum peak (λ_{max}) at 605 nm and the CIE coordinates are (0.58, 0.41). The maximum power efficiency of this device is 0.38 lm W⁻¹, which is much lower than that of C1-based devices. The performances of the two devices are listed in Table S4.



Figure. S7. The Luminance (L)–current density (J) and the Luminous efficiency (LE)–current density (J) characteristics of L1 and C1-based devices with the configuration ITO/ PEDOT:PSS/PVK/EML (~60 nm)/CsF (0.5nm)/Al (120 nm)

Figure S7 shows the luminance (L)-current density (J) and luminous efficiency (LE)-current density (J) characteristics of the devices based on C1 and L1, respectively. The luminance and luminous efficiency at the same voltage of the C1-based device are larger than those of the L1-based device. There are many microcrystal boundaries in the L1 layer, which act as not only the carriers-scatting centers but also the nonradiating recombination centers. So the luminance and

luminance efficiency of the L1-based device are lower. C1 has a higher T_g , and morphologically more-stable film, which can benefit the lifetime of the device based on it.

 Table S4: EL performance of the solution-processed small-mocules devices

 based on L1 and C1.

Device	C1	L1	
Turn-on Voltage [V] ^{a)}	4.0	4.4	
LE^{b} [cd A^{-1}]	0.34@4.75V	0.19@5.10V	
EQE ^{d)} [%]	0.67@4.75V	0.38@5.10V	
$L_{max}^{e)}$ [cd m ⁻²]	761@9.75V	324@8.70V	
CIE@7V	(0.59,0.41)	(0.58,0.41)	

^{a)}Defined as the voltage at which the luminance is about 1 cd/m², ^{b)}Maximum luminous efficiency, ^{c)}Maximum power efficiency, ^d)External quantum efficiency, ^{e)}Maximum luminance. Device structure of ITO/PEDOT:PSS (40 nm)/PVK (40 nm)/EML (~60 nm)/CsF (1.5 nm)/Al (120 nm).