Supplementary Information

Novel Dopant-Free Carbazole and Phenothiazine-Appended Indolo [3,2-a]carbazole-Based Small Molecules as Efficient Hole-Transport Materials for Perovskite Solar Cell

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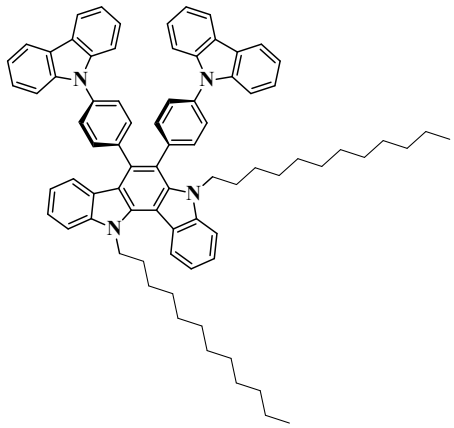
TABLE OF CONTENTS

CHARACTERIZATION OF HTMS

Synthesis of 6,7-bis(4-(9H-carbazol-9-yl)phenyl)-5,12-didodecyl-5,12-dihydroindolo[3,2-a]carbazole (C_{12}Cbz-IC, 1)



Chemical formula: $C_{78}H_{82}N_4$

Yield: 75 %

m.p: 162 ^oC

Appearance: Colourless Solid

IR (KBr): ν_{max} (cm^{-1}) = 2926 (C-H), 1456 (C=C), 1329 (C-N).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.51 (d, 1H, J=8 Hz), 8.17 (t, 4H, J=7 Hz), 7.63 (d, 4H, J=8 Hz), 7.60-7.52 (m, 7H), 7.44-7.38 (m, 4H), 7.34-7.24 (m, 10H), 7.05 (t, 1H, J=7.6 Hz), 6.82 (d, 1H, J=8 Hz), 4.99 (d, 2H, J=8 Hz), 4.06 (d, 2H, J=8.4 Hz), 2.29 (s, 2H), 1.65-1.62 (m, 4H), 1.48 (s, 2H), 1.36-1.24 (m, 14H), 1.18-1.52 (m, 16H), 1.05 (s, 2H), 0.92-0.84 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 146.5, 146.2, 146.0 (2C), 144.9, 143.5, 143.2, 141.7, 141.5, 141.3, 140.4, 138.7, 137.2, 131.9, 131.3 (2C), 129.7, 129.5, 129.1, 128.6, 128.5, 127.7, 126.3, 126.2, 125.5, 125.1 (2C), 124.6, 124.5, 122.4, 120.3, 114.8, 114.6, 114.5, 113.0, 51.8, 50.1, 37.1, 37.0, 36.2, 34.8, 34.7 (2C), 34.6, 34.5 (2C), 34.0, 32.2, 32.1, 27.9, 27.8.

MALDI- TOF MS (ESI MS) m/z: $[M+H]^+$ calculated for $C_{78}H_{82}N_4$ 1075.6618, found 1075.3520.

^{1}H AND ^{13}C NMR SPECTRA OF HTMS

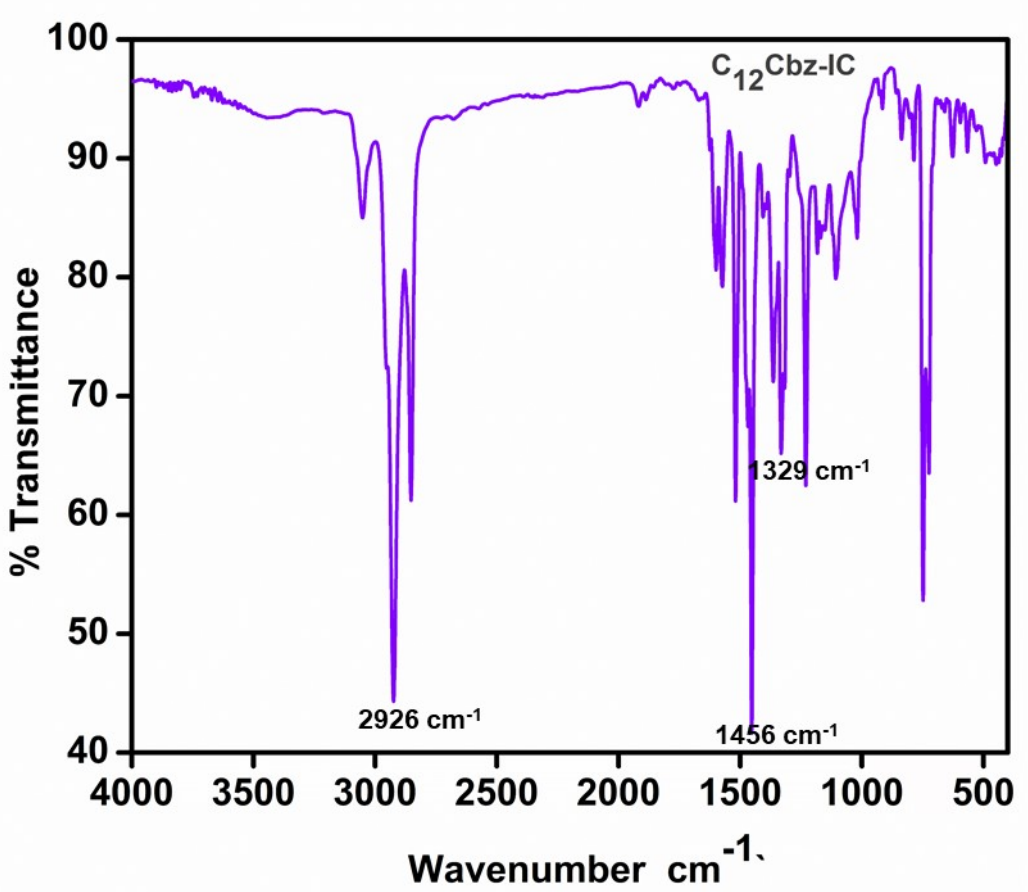


Figure S1. IR spectra of C_{12}Cbz-IC molecule.

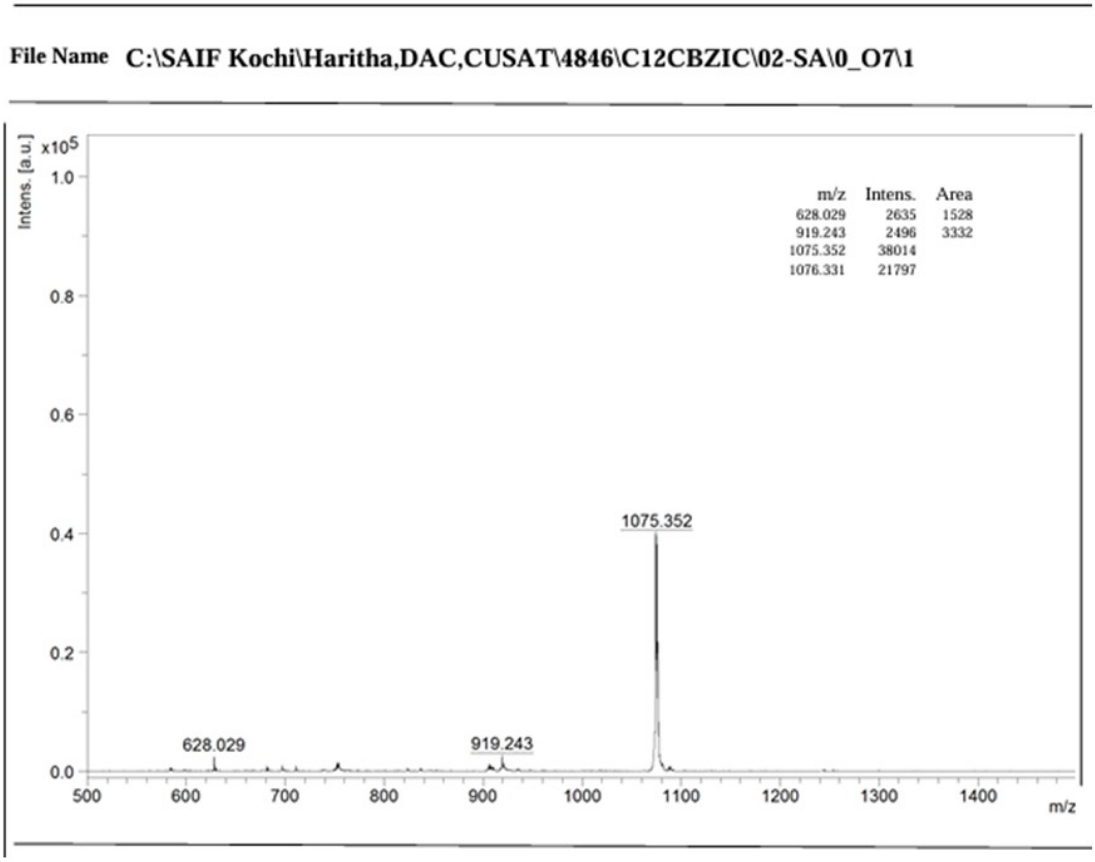


Figure S2. MALDI-TOFF mass spectra of C_{12}Cbz-IC molecule.

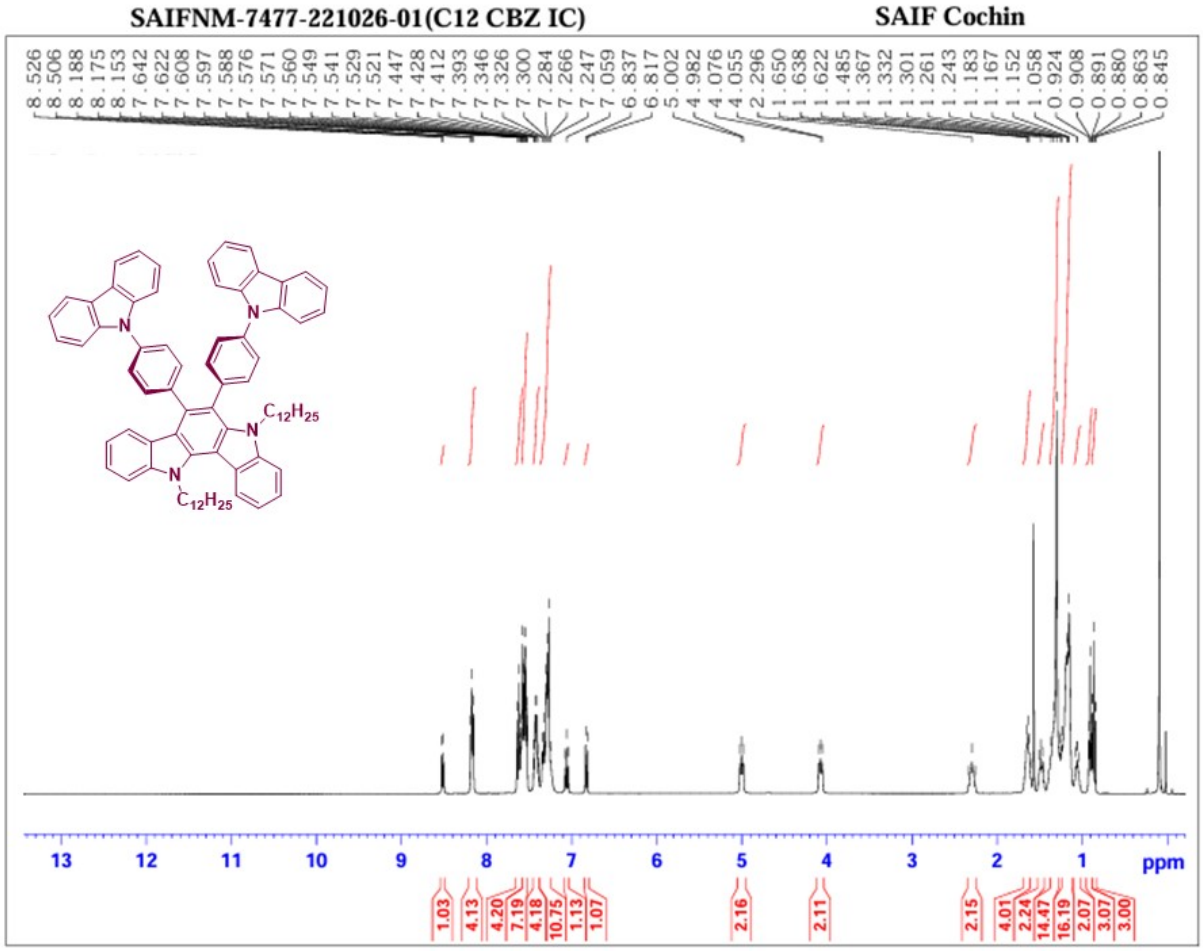


Figure S3. ^{1}H NMR spectra of C_{12}Cbz-IC molecule.

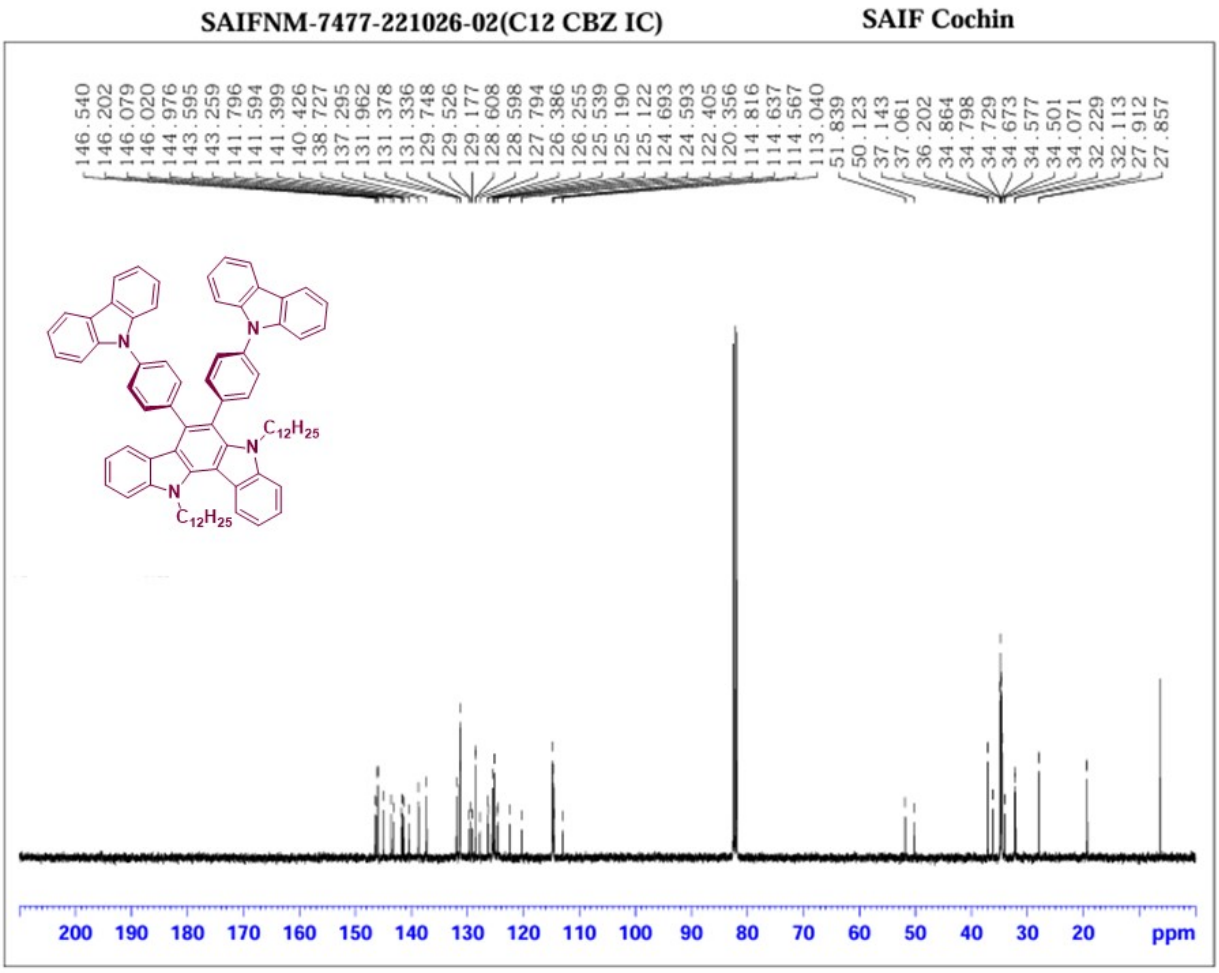
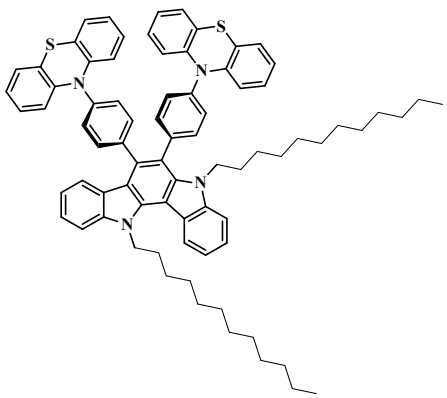


Figure S4. ^{13}C NMR spectra of C_{12}Cbz-IC molecule

Synthesis of 10,10'-((5,12-didodecyl-5,12-dihydroindolo[3,2-a]carbazole-6,7-diyl)bis(4,1-phenylene))bis(10H-phenothiazine) (C_{12}Phz-IC, 2)



Chemical formula: $C_{78}H_{82}N_4S_2$

Yield: 78 %

m.p: 138 ^{0}C

Appearance: Colourless Solid

FT-IR (KBr): ν_{max} (cm^{-1}) = 2918 (C-H), 1463 (C=C), 1307 (C-N), 734 (C-S).

^{1}H NMR (400 MHz, CDCl3, δ ppm): 8.48 (d, 1H, J=8.4 Hz), 7.58-7.49 (m, 7H), 7.39 (d, 4H, J= 7.6 Hz), 7.32 (d, 2H, J=7.6 Hz), 7.00 (d, 4H, J=6.4 Hz), 6.96 (d, 1H, J=7.2 Hz), 6.80 (d, 1H, J=7.2 Hz), 6.76-6.68 (m, 8H), 6.28 (t, 2H, J=4.4 Hz), 6.20 (d, 2H, J=7.6 Hz), 4.97 (t, 2H, J=8 Hz), 4.01 (t, 2H, J=8 Hz), 2.26 (s, 2H), 1.61-1.54 (m, 6H), 1.46 (t, 2H, J=6.8 Hz), 1.32-1.14 (m, 28H), 0.99 (t, 2H, J=6.8 Hz), 0.91-0.85 (m, 6H).

^{13}C NMR (100 MHz, CDCl3, δ ppm): 149.2, 149.1, 146.5, 146.2, 145.7, 145.1, 144.8, 144.1, 143.2, 141.8, 140.0, 139.5, 138.2, 135.7, 134.7, 132.2, 132.1, 131.9, 131.8, 129.7, 129.4, 129.1, 127.7, 127.6, 126.4, 126.2, 125.9, 125.5, 124.7, 124.3, 122.2, 121.4, 121.2, 114.8, 114.6, 113.2, 51.8, 50.0, 37.1, 37.0, 36.1, 34.8, 34.7 (2C), 34.6, 34.5 (2C), 32.0, 31.8, 27.8 (2C), 19.2.

MALDI- TOF MS (ESI MS) m/z: $[M+H]^+$ calculated for $C_{78}H_{82}N_4S_2$ 1139.6059, found 1139.5900.

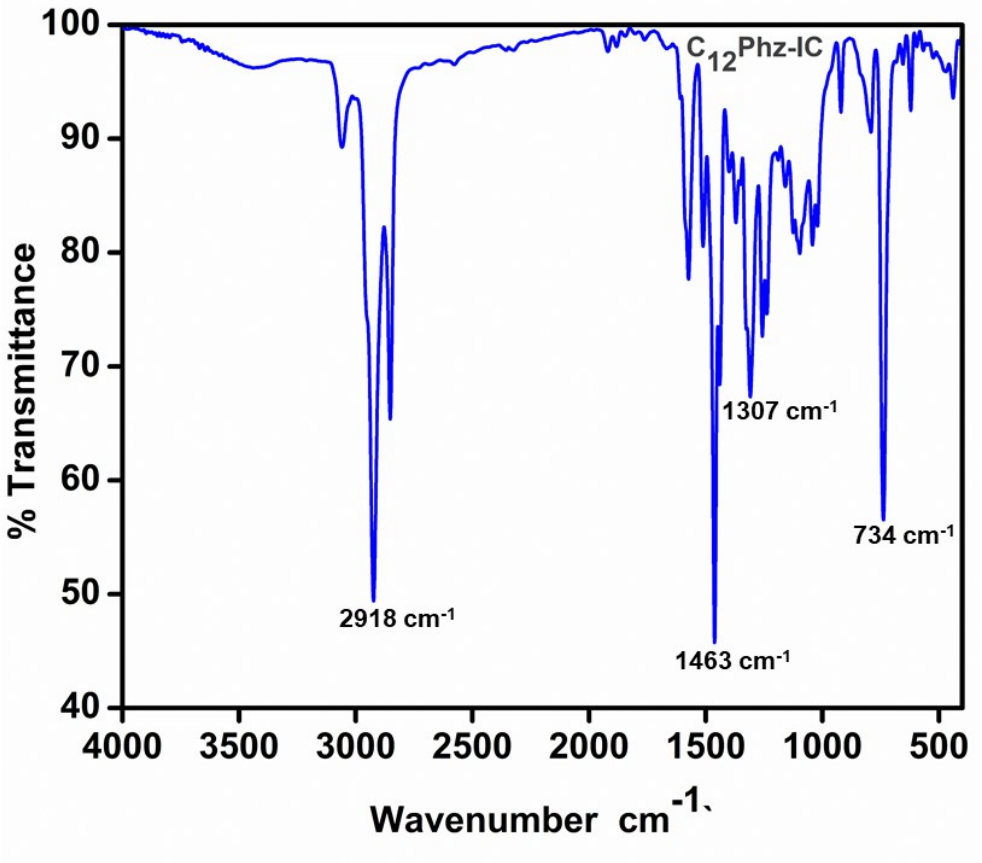


Figure S5. IR spectra of C_{12}Phz-IC molecule.

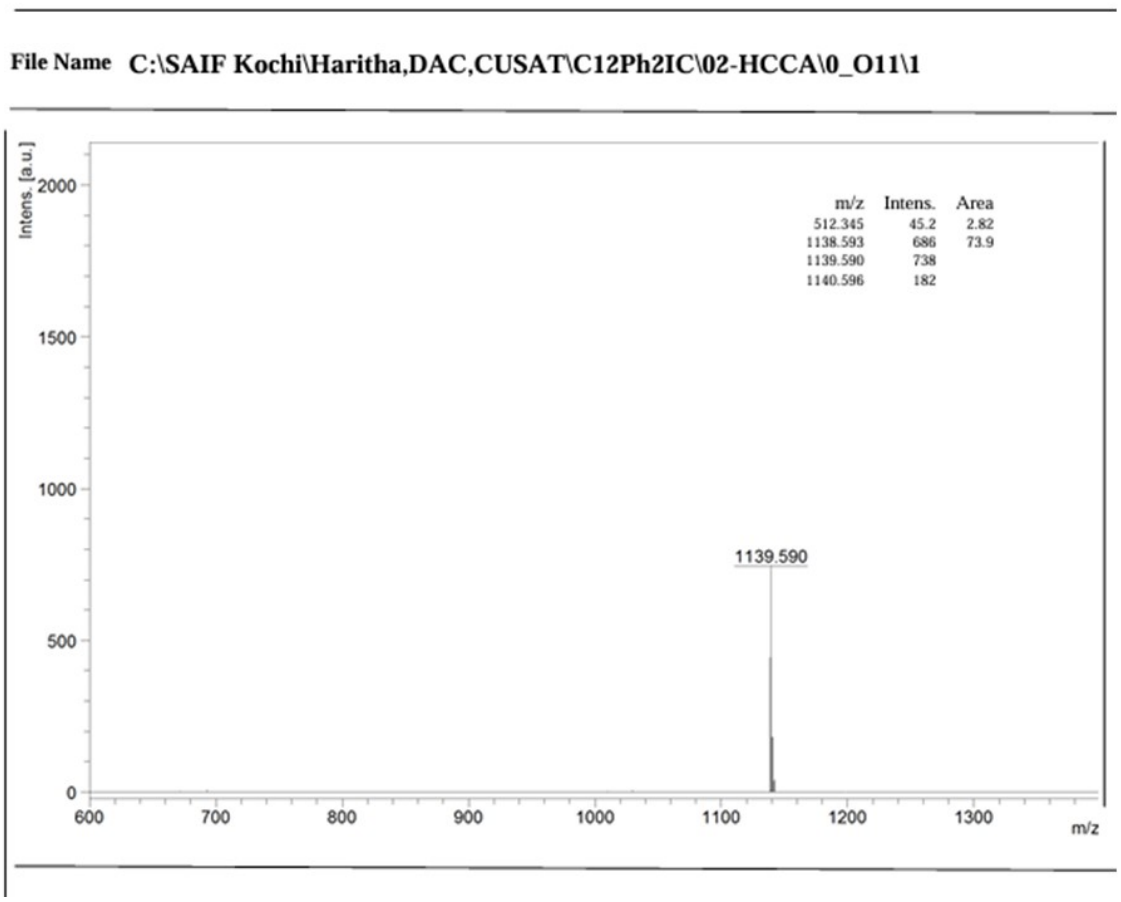


Figure S6. MALDI-TOFF mass spectra of C_{12}Phz-IC molecule.

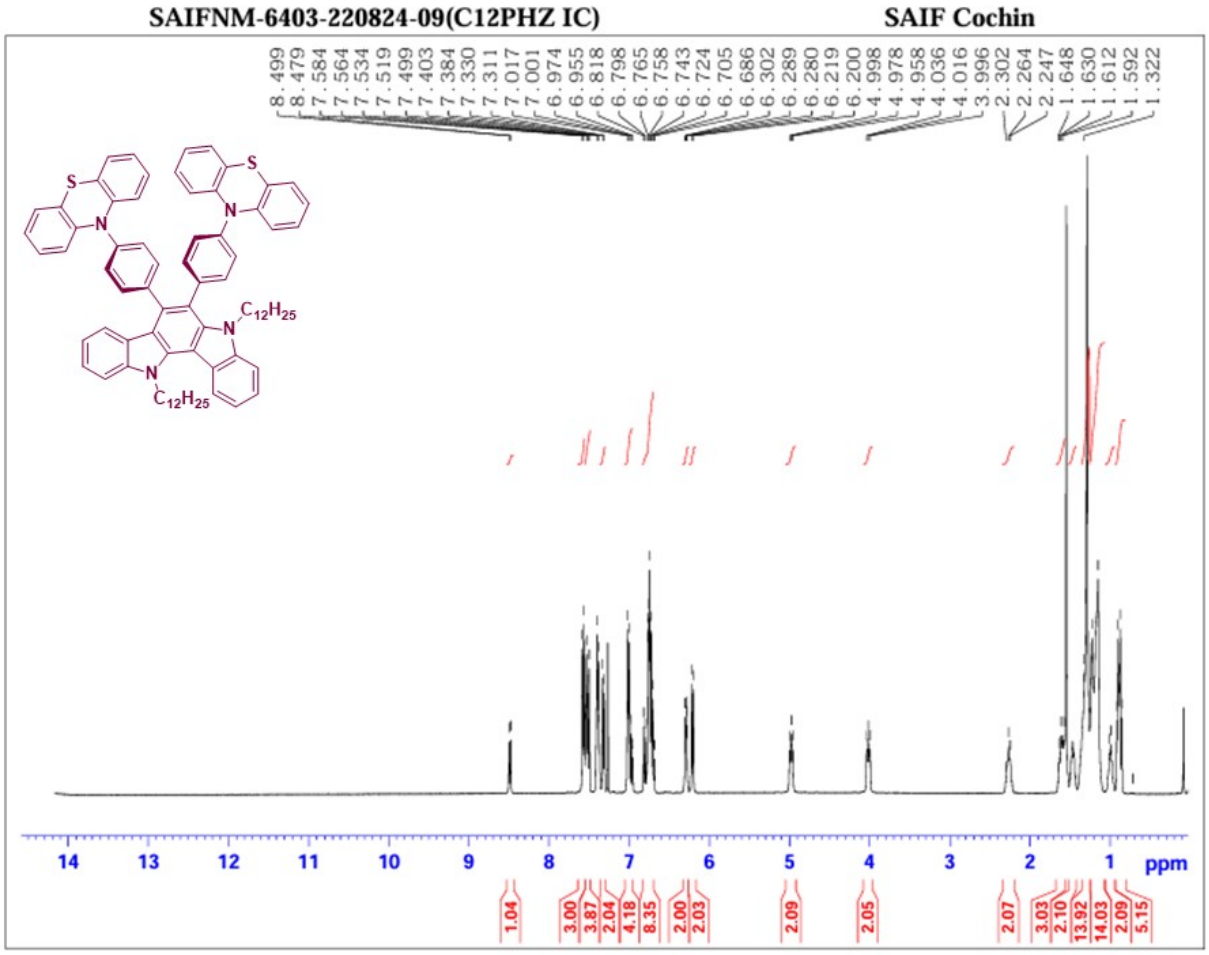


Figure S7. ^{1}H NMR spectra of C_{12}Phz-IC molecule.

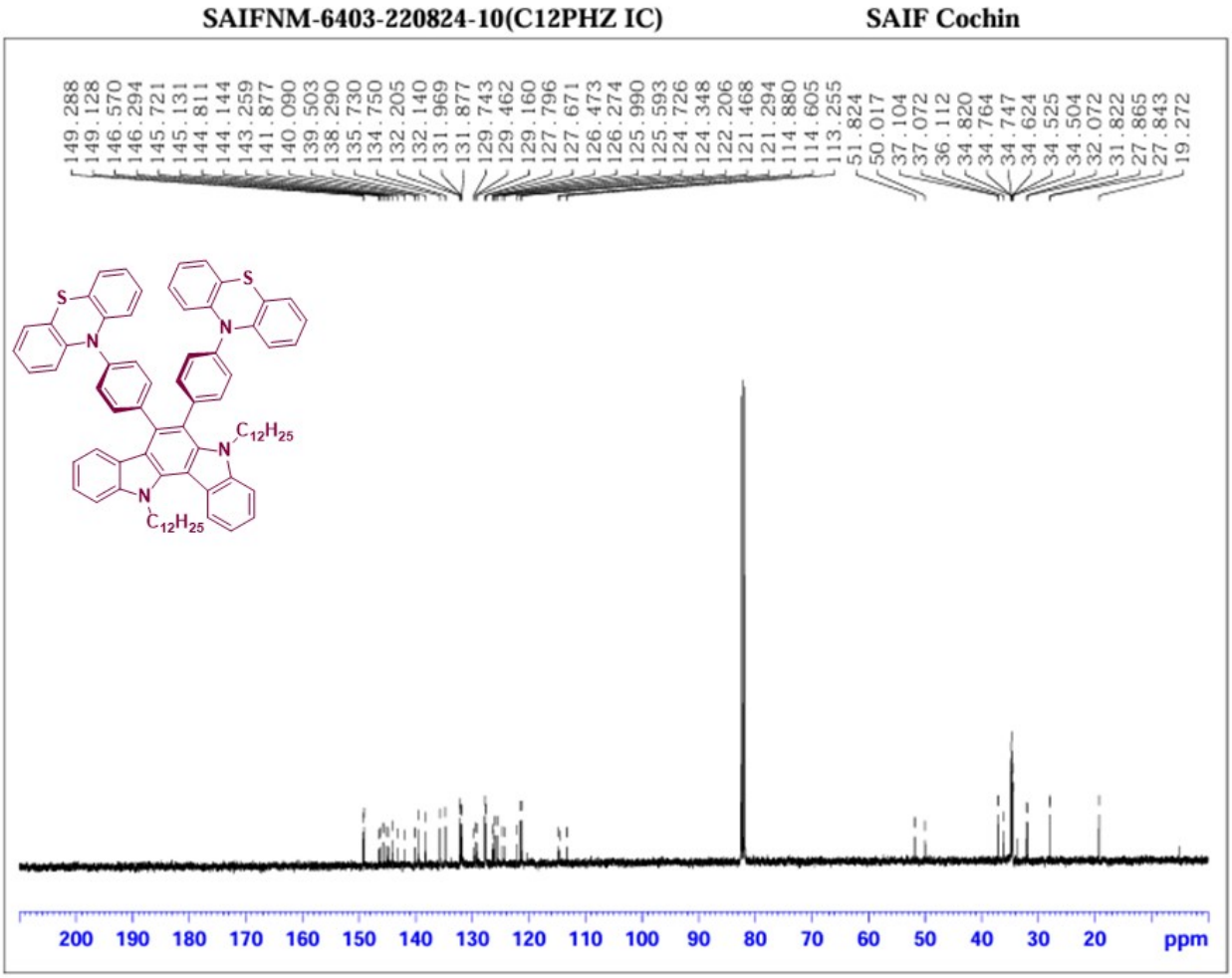


Figure S8. ^{13}C NMR spectra of C_{12}Phz-IC molecule.

SUPPORTING SCHEMES, FIGURES AND TABLES

Table S1. Calculated dihedral angles (°) of indolocarbazole molecules after geometry optimization.

IC-based HTMs	Dihedral angles (°) (ϕ_1= C_{13}-C_{14}-C_{27}-C_{29})	Dihedral angles (°) ($\phi_{2=}$ C_{15}-C_{16}-C_{37}-C_{38})
C_{12}Cbz-IC	80	85
C_{12}Phz-IC	89	82

Table S2. Energy level parameters of HTMs

HTM	HOMO (eV)	LUMO (eV)	Energy band gap (Eg) (eV)
C_{12}Cbz-IC	-5.36	-1.21	4.15
C_{12}Phz-IC	-5.16	-1.27	3.89

Intersection of the absorption and emission spectra of C_{12}Cbz-IC, C_{12}Phz-IC and Spiro-OMeTAD

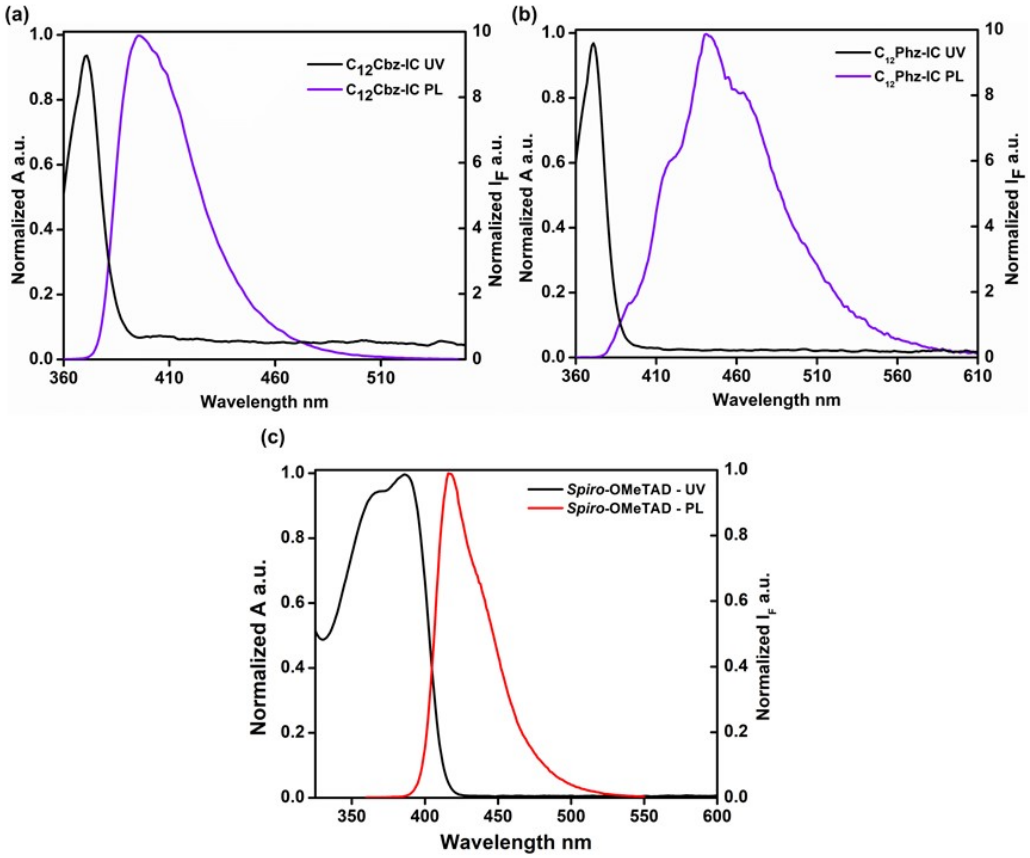


Figure S9. The intersection of UV-Vis absorption and fluorescence emission spectra of (a). C_{12}Cbz-ICs and (b). C_{12}Phz-ICs and (c). Spiro-OMeTAD recorded in 10^{-5} M THF solution.

Grazing-incidence X-ray diffraction pattern of HTMs

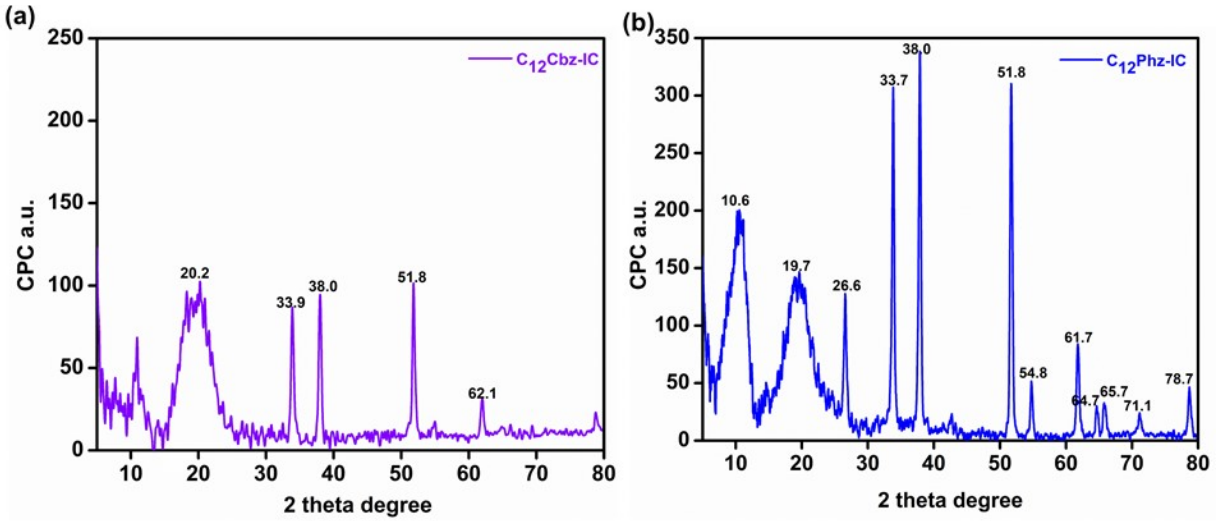


Figure S10. The Grazing-incidence X-ray diffraction pattern of (a). C_{12}Cbz-IC, (b). C_{12}Phz-IC on FTO substrate.

SEM images of C_{12}Cbz-IC and C_{12}Phz-IC

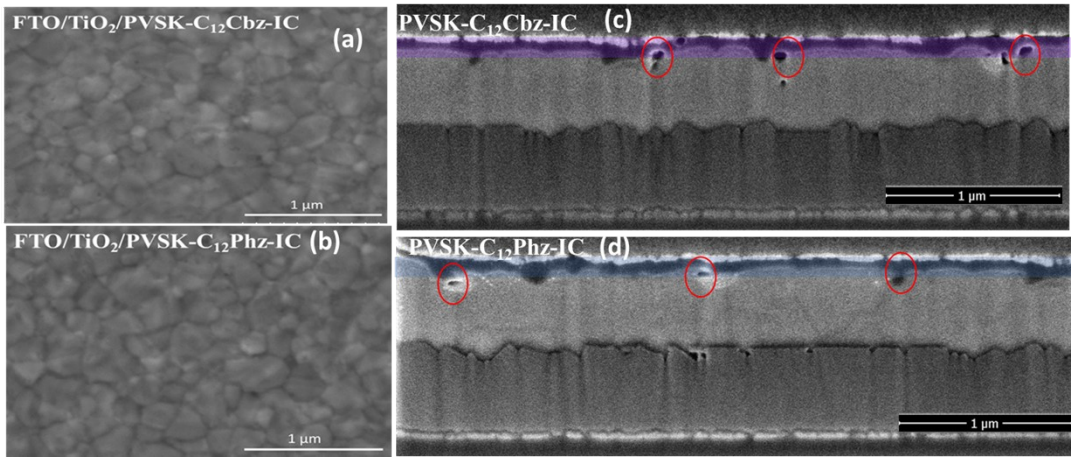


Figure S11. (a, b) Top-view SEM images of C_{12}Cbz-IC and C_{12}Phz-IC HTM layers deposited on the PVSK layer, respectively. (c, d) Cross-sectional SEM images of C_{12}Cbz-IC and C_{12}Phz-IC on PVSK/FTO films.

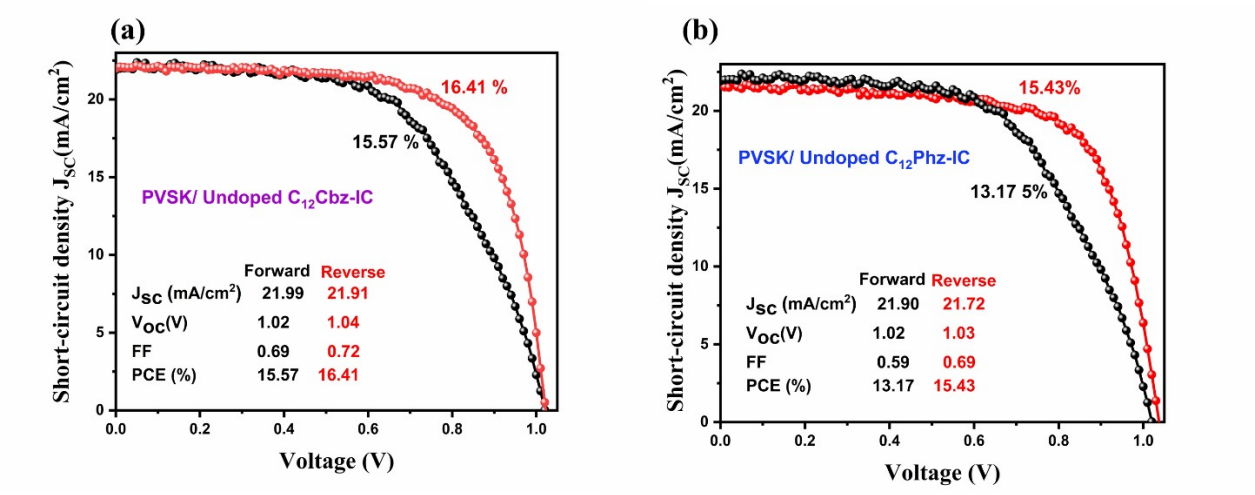


Figure S12. Forward and reverse J–V curves of PSCs based on C_{12}Cbz-IC and C_{12}Phz-IC, respectively.

External quantum efficiency of C_{12}Cbz-IC and C_{12}Phz-IC

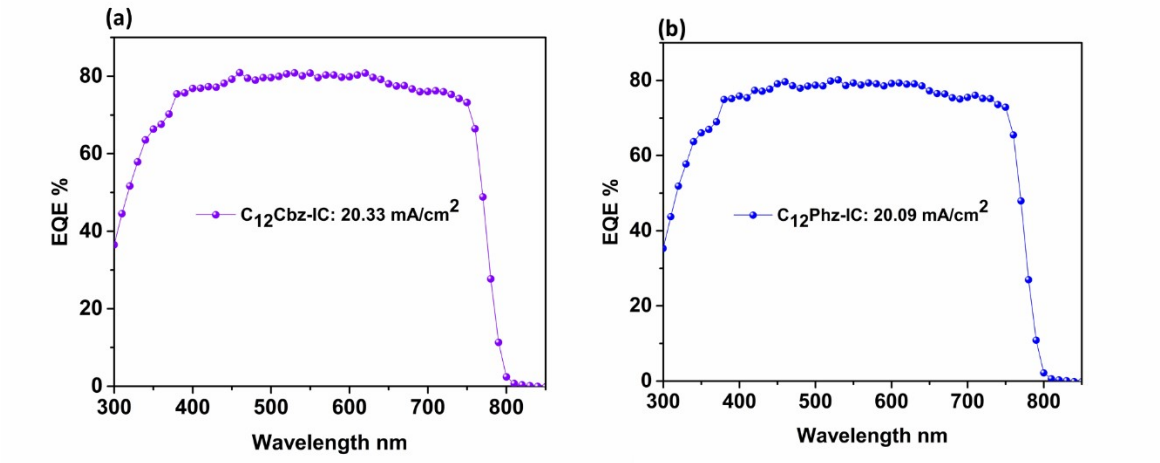


Figure S13. EQE of C_{12}CbZ-IC and C_{12}Phz-IC-based PSCs, respectively.

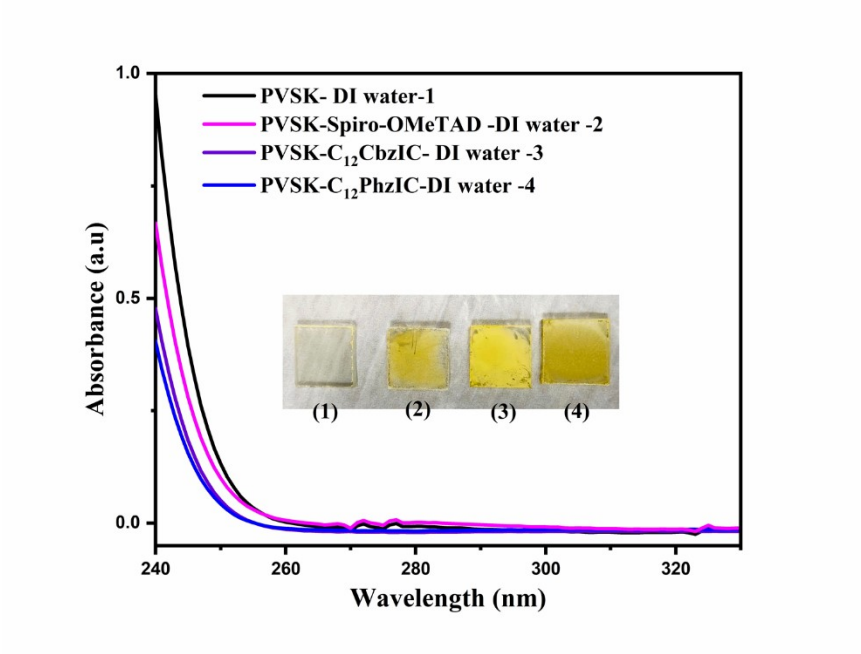


Figure S14. UV–vis absorption spectra and corresponding photographs of pristine PVSK, PVSK/Spiro-OMeTAD, PVSK/C12Cbz-IC, and PVSK/C12Phz-IC films after immersion in deionized water for 10 min.

COST CALCULATION FOR HTMs

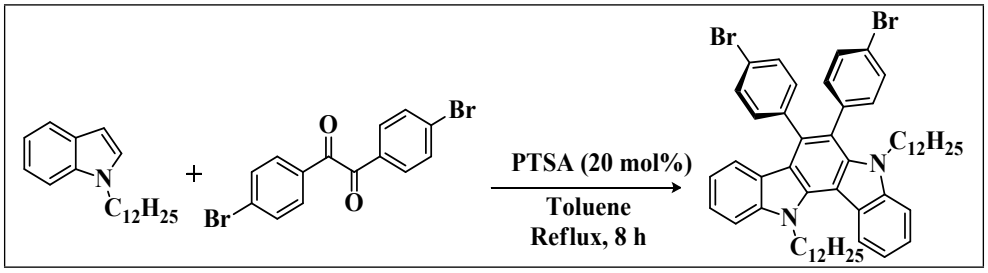
Cost calculation for C_{12}Cbz-IC

1. **Synthesis of 1-dodecyl-1H-indole (3)**

Chemicals/company	Price ($) (g or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
1H-indole (Sigma-	1.10 $/g	0.50			0.55

Aldrich)					
1-bromododecane (Sigma-Aldrich)	**0.52 $/g**	**1.28**			**0.67**
Potassium hydroxide (Sigma-Aldrich)	**1.40 $/g**	**0.60**			**0.84**
Dimethyl sulfoxide (Sigma-Aldrich)	**529.20 $/L**		**20**		**10.58**
***n*-Hexane (Sigma-Aldrich)**	**94.05 $/L**			**20**	**1.88**
Total					**14.52**

2. **Synthesis of 6,7-bis(4-bromophenyl)-5,12-didodecyl-5,12-dihydroindolo[3,2-*a*]carbazole (5)**



Chemicals/company	**Price ($) (g or mL)**	**Chemicals used for batch preparation**			**Chemical cost ($)**
		Reagent (in g)	**Solvent (in ml)**	**Workup (in g or ml)**	
1-dodecyl-1H-indole	**-**	**0.50**			**14.52**
4,4'dibromobenzil (Sigma-Aldrich)	**1.33 $/g**	**0.32**			**0.43**
Para-toluenesulfonic acid (Sigma-Aldrich)	**0.54 $/g**	**0.06**			**0.03**
Toluene (Sigma-Aldrich)	**50.05 $/L**		**10**		**0.50**
Total					**15.48**

3. **Synthesis of 6,7-bis(4-(9H-carbazol-9-yl)phenyl)-5,12-didodecyl-5,12-dihydroindolo[3,2-*a*]carbazole (C_{12}Cbz-IC, 1)**

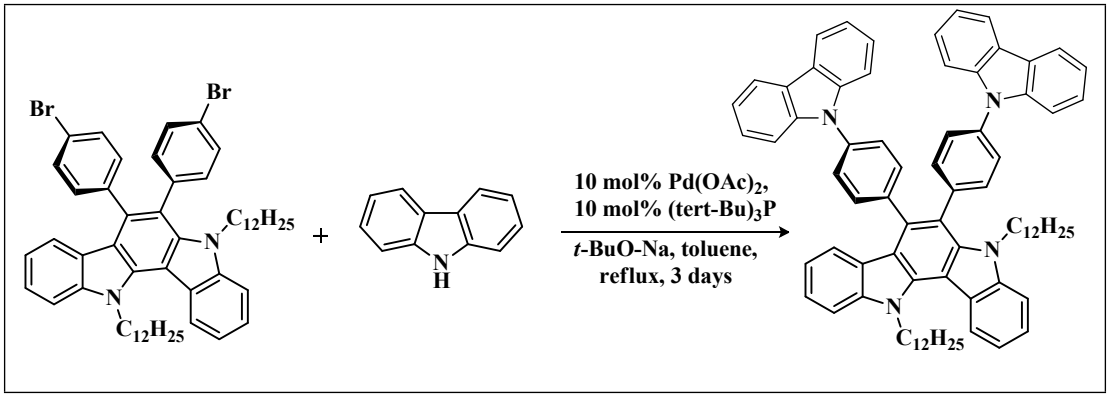


Table S3. Material cost evaluation of C_{12}Cbz-IC

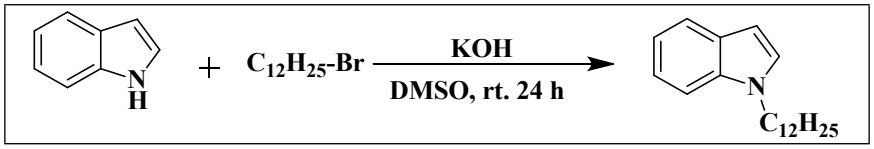
Chemicals/company	Price ($) (g or mL)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
6,7-bis(4-bromophenyl)-5,12-didodecyl-5,12-dihydroindolo[3,2-*a*]carbazole (Sigma-Aldrich)	-	0.50			15.48
Carbazole (Sigma-Aldrich)	0.44 $/g	0.28			0.12
Sodium tert-butoxide (Sigma-Aldrich)	15.79 $/g	0.22			3.47
Palladium(II)acetate (Sigma-Aldrich)	111.73 $/g	0.011			1.23
Tri-tert-butylphosphine (Spectrochem) (Sigma-Aldrich)	40.40 $/g	0.012			0.48
Toluene (Sigma-Aldrich)	50.05 $/L		6		0.30
Dichloromethane (Sigma-Aldrich)	86.59 $/L			20	1.73
Total					22.81

C_{12}Cbz-IC: Yield, 78%, 0.465 g, 22.81 $

The cost of 1 g of C_{12}Cbz-IC is 49.053 $

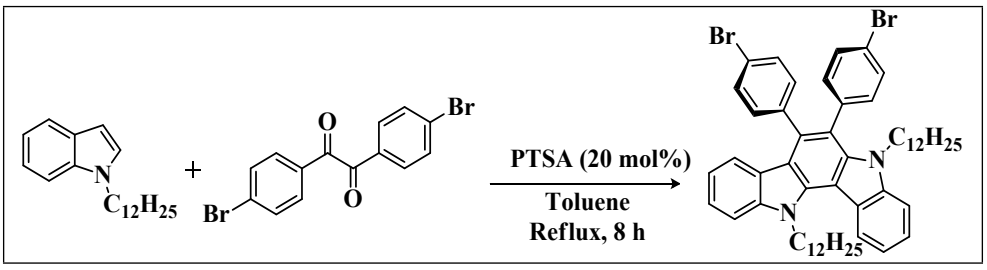
Cost calculation for C_{12}Phz-IC

1. **Synthesis of 1-dodecyl-1H-indole (3)**



Chemicals/company	Price ($) (g or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
1H-indole (Sigma-Aldrich)	1.10 $/g	0.50			0.55
1-bromododecane (Sigma-Aldrich)	0.52 $/g	1.28			0.67
Potassium hydroxide (Sigma-Aldrich)	1.40 $/g	0.60			0.84
Dimethyl sulfoxide (Sigma-Aldrich)	529.20 $/L		20		10.58
n-Hexane (Sigma-Aldrich)	94.05 $/L			20	1.88
Total					14.52

2. **Synthesis of of 6,7-bis(4-bromophenyl)-5,12-didodecyl-5,12-dihydroindolo[3,2-*a*]carbazole (5)**



Chemicals/company	Price ($) (g or mL)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
1-dodecyl-1H-indole	-	0.50			14.52
4,4'dibromobenzil (Sigma-Aldrich)	1.33 $/g	0.32			0.43
Para-toluenesulfonic acid (Sigma-Aldrich)	0.54 $/g	0.06			0.03
Toluene (Sigma-Aldrich)	50.05 $/L		10		0.50
Total					15.48

3. Synthesis of 10,10'-((5,12-didodecyl-5,12-dihydroindolo[3,2-*a*]carbazole-6,7-diyl)bis(4,1-phenylene))bis(10H-phenothiazine) (C_{12}Phz-IC, 2)

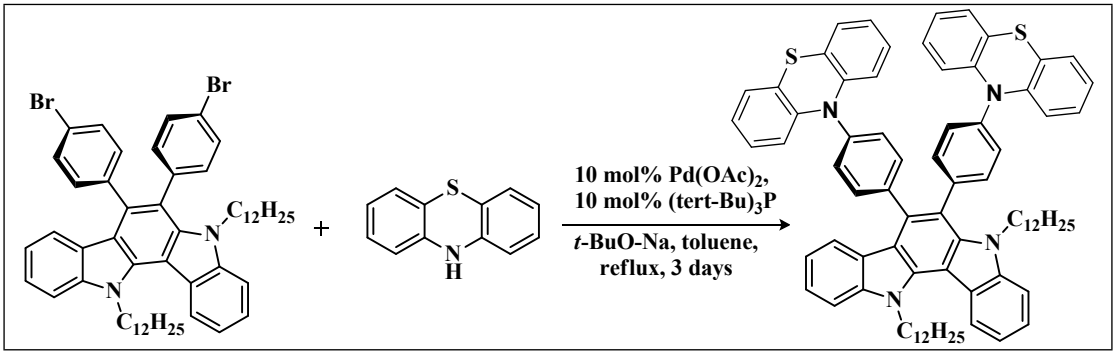


Table S4. Material cost evaluation of C_{12}Phz-IC

Chemicals/company	Price ($) (g or mL)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
6,7-bis(4-bromophenyl)-5,12-didodecyl-5,12-	-	0.50			15.48

dihydroindolo[3,2-*a*]carbazole					
Phenothiazine (Sigma-Aldrich)	**0.77**	**0.33**			**0.25**
Sodium tert-butoxide (Sigma-Aldrich)	**15.79**	**0.22**			**3.47**
Palladium(II) acetate (Sigma-Aldrich)	**111.73**	**0.011**			**1.23**
Tri-tert-butylphosphine (Sigma-Aldrich)	**40.40**	**0.012**			**0.48**
Toluene (Sigma-Aldrich)	**50.05**		**6**		**0.30**
Dichloromethane (Sigma-Aldrich)	**86.59**			**20**	**1.73**
Total					**22.94**

C_{12}Phz-IC: Yield, 78%, 0.495 g, 22.94 $

The cost of 1 g of C_{12}Phz-IC is 46.343 $

Cost of Spiro-OMeTAD (1g): 568.31$ (according to Sigma-Aldrich, CAS No: 207739-72-8)