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High-efficiency organic solar cells enabled by non-ionic small-molecule cathode interlayers with tunable alkoxy side chains †

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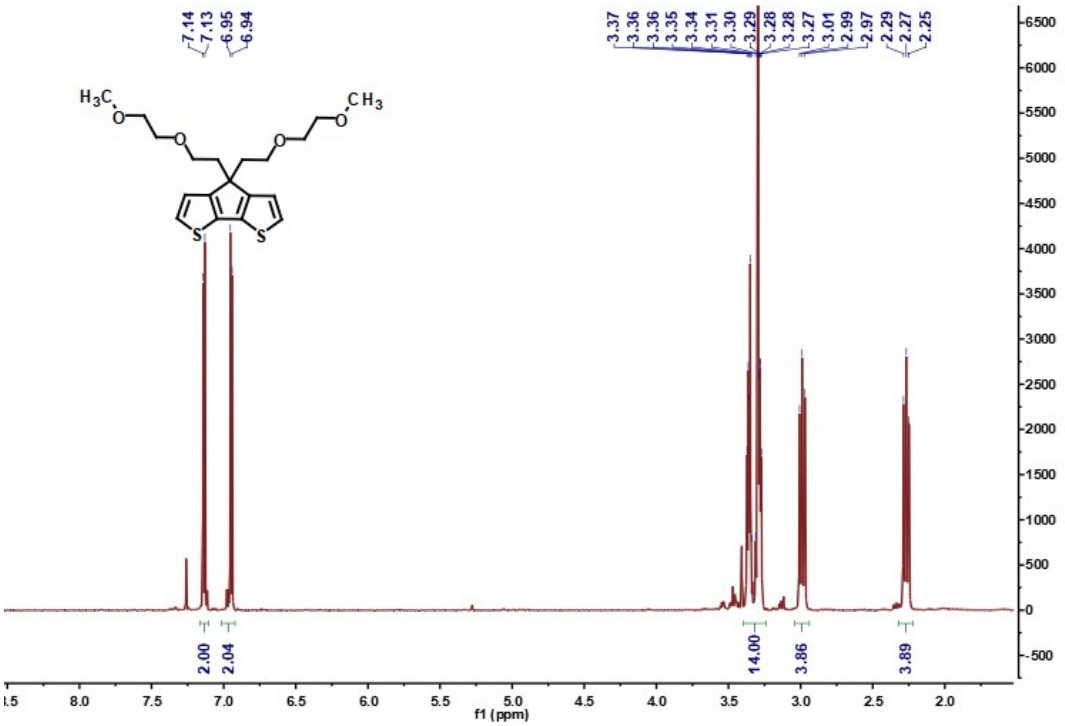

Figure S1. ^{1}H NMR of 1a

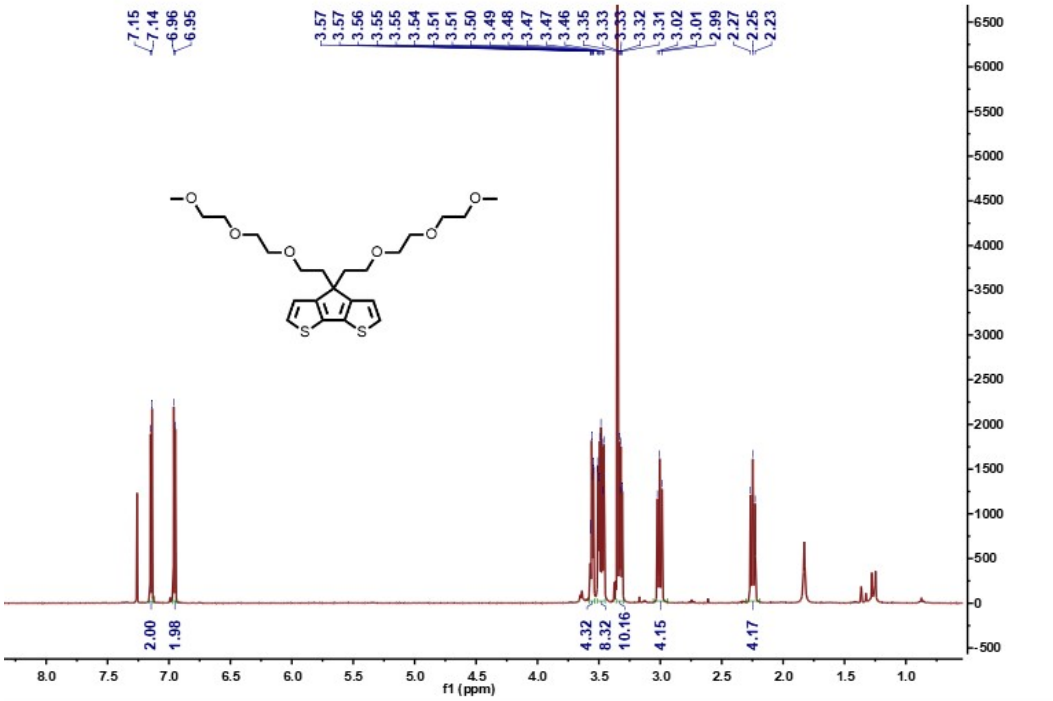

Figure S2. ^{1}H NMR of 1b

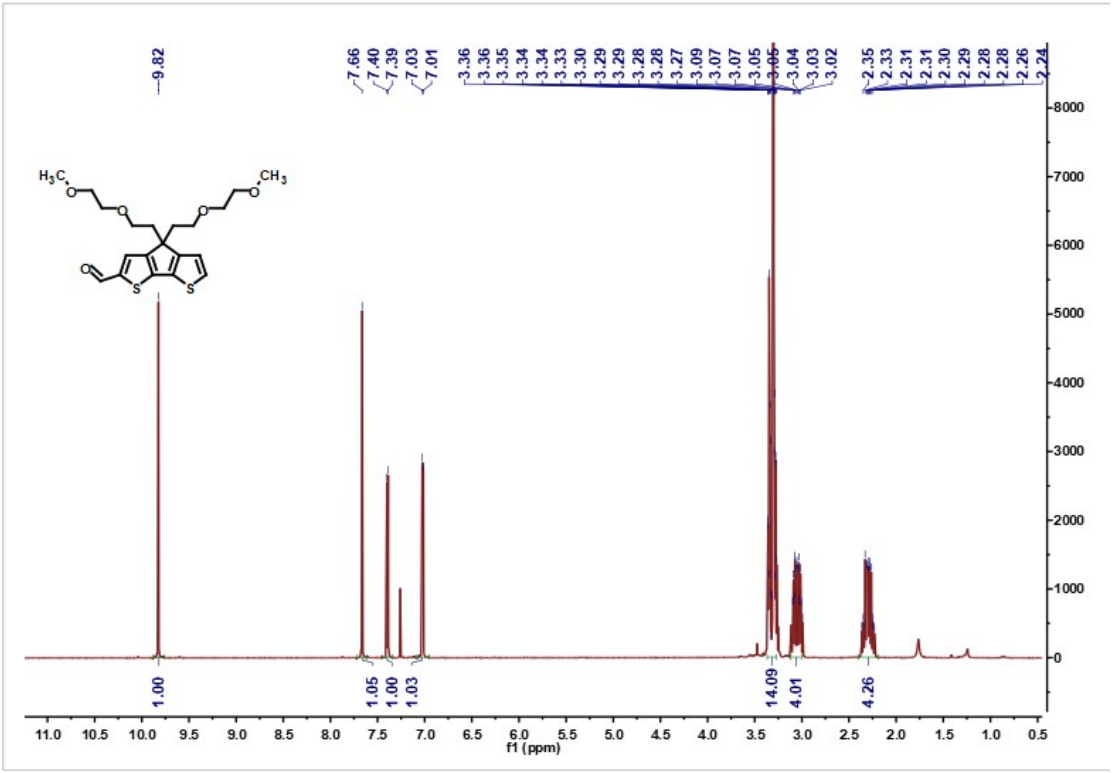

Figure S3. [1]H NMR of 2a

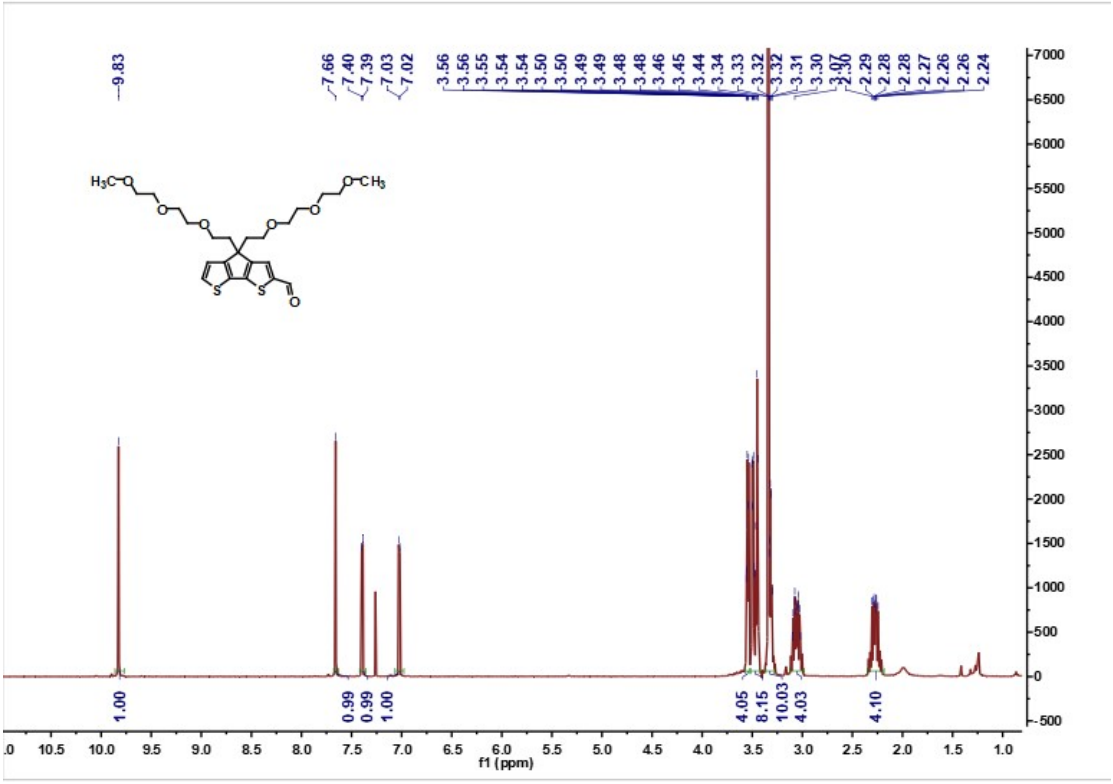

Figure S4. [1]H NMR of 2b

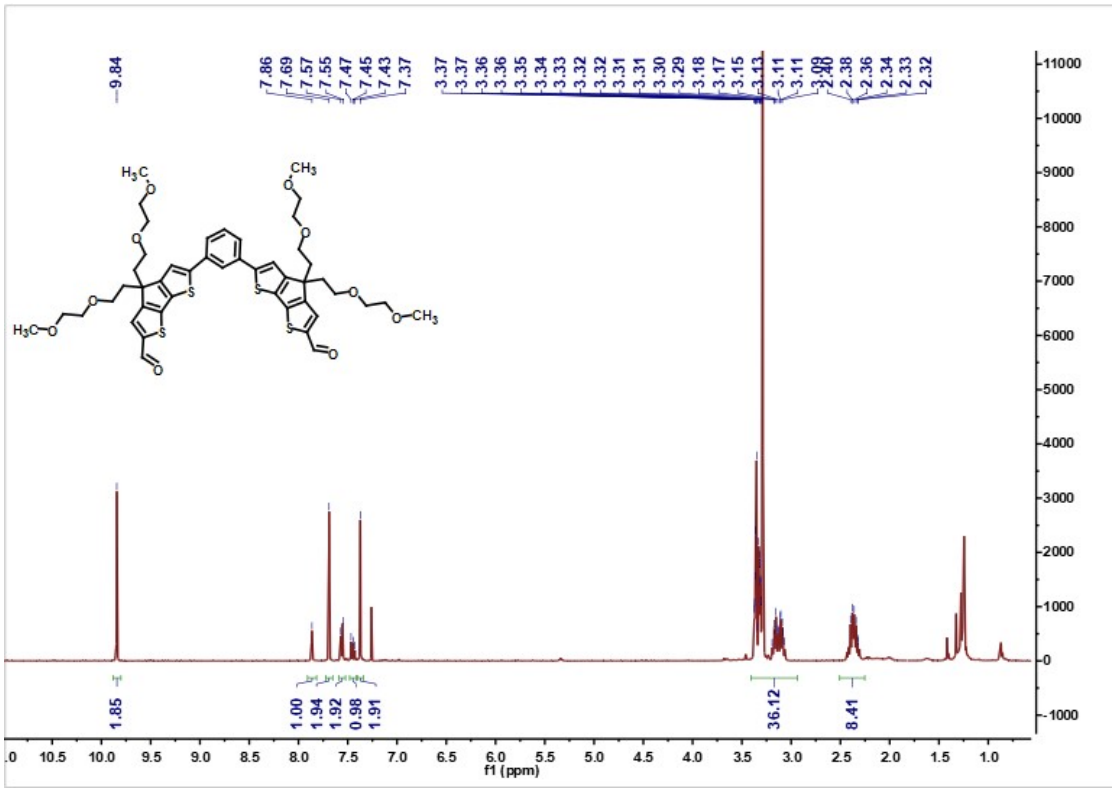

Figure S5. 1H NMR of 3a

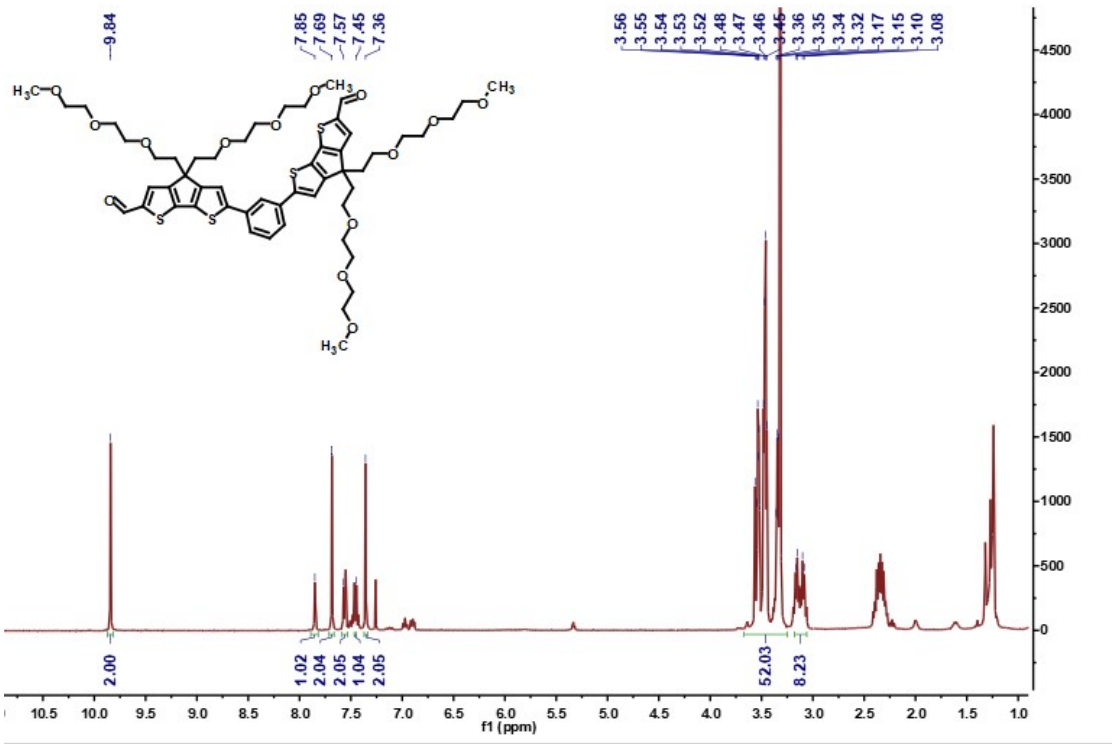

Figure S6. 1H NMR of 3b

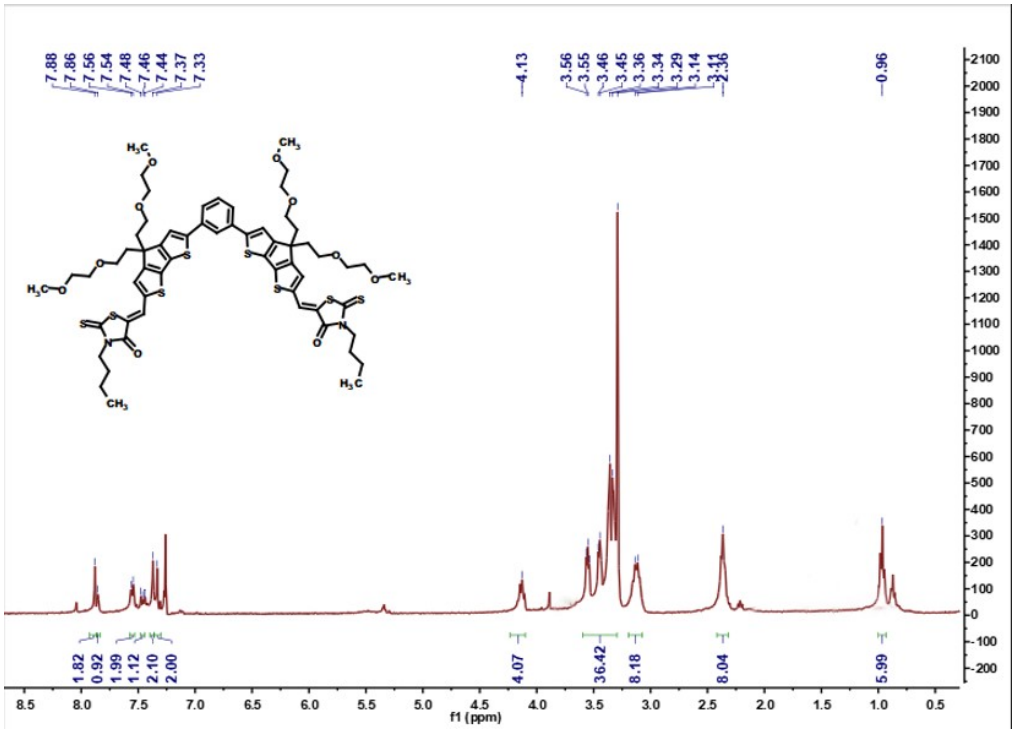

Figure S7. ^{1}H NMR of **M-*d*OR**

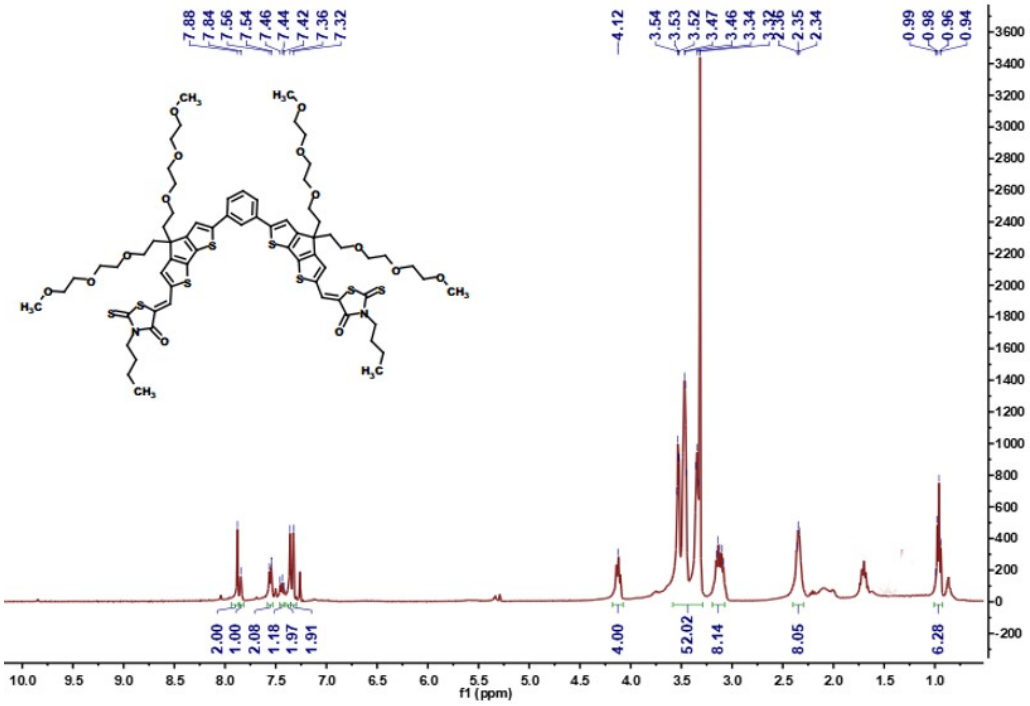

Figure S8. ^{1}H NMR of **M-*t*OR**

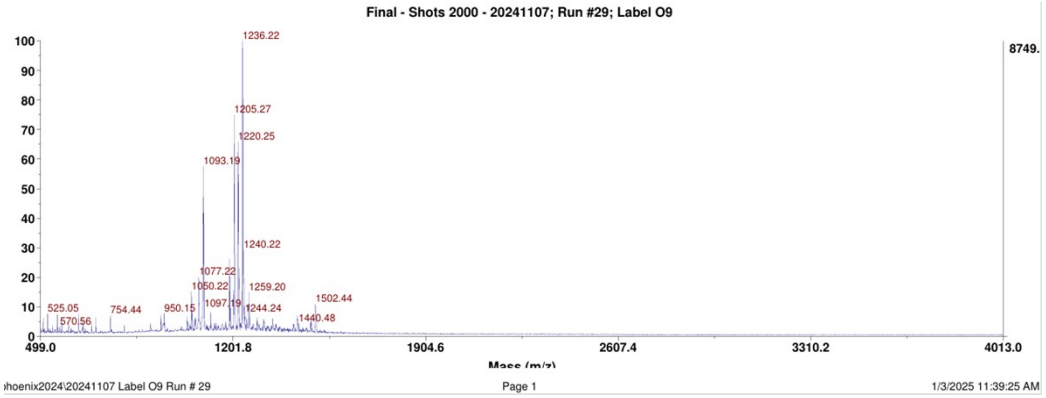

Figure S9. MLADI-TOF of **M-*d*OR**

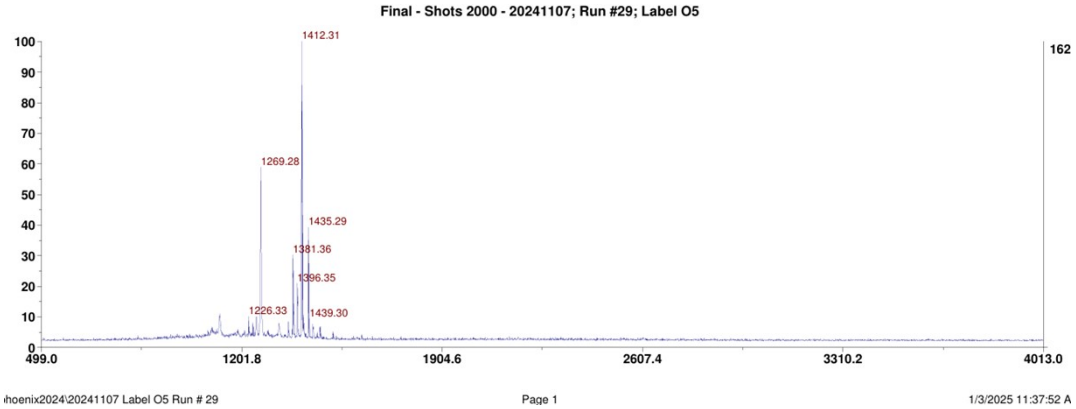

Figure S10. MLADI-TOF of **M-*t*OR**

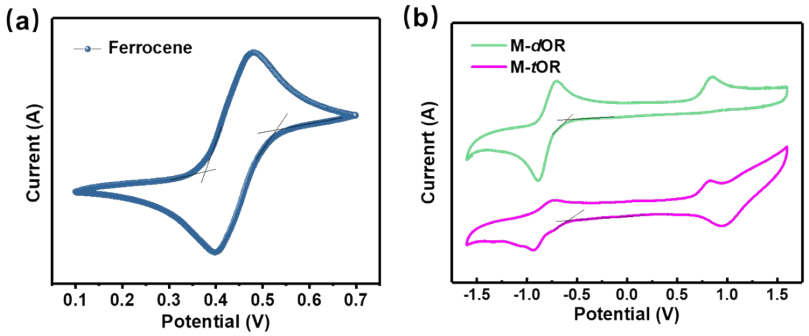

Figure S11. CV curves of (a) standard, (b) M-*d*OR and M-*t*OR

Device fabrication

Organic photovoltaics were fabricated on glass substrates pre-coated with a layer of indium tin oxide (ITO) with the structure of ITO/PEDOT:PSS/Active layer/CIL/Ag. Before fabrication, the substrates were subjected to a series of cleaning agents including detergent, deionized water, acetone, and isopropanol, with each step lasting for 20 minutes. Subsequently, the pre-treated ITO substrates were exposed to an ultraviolet ozone generator for a duration of 6 minutes, followed by being spin-coating of PEDOT:PSS (CleviosTM 4083) at 4500 rpm. After baking the PEDOT:PSS layer in air at 135℃ for 10 min, the substrates were transferred into the N_2 glovebox to ensure a controlled environment. For all blends, the total concentration was maintained at 16

mg·ml-1 dissolved in chloroform, with a fixed donor-acceptor (D:A) weight ratio of 1:1.25, 0.5% (v/v) CN as additive and spin-coated in a nitrogen glove box at 3000 rpm for 40 s, and then were annealed at 100°C, 10min. After that, the TFE solution of **M-*d*OR** (0.25 mg/mL)/**M-*t*OR** (0.25 mg/mL)/PDINO (1.0 mg/mL) was spin-coated at 3500r/3000r; Finally, thermal evaporation was employed to deposit a 100 nm-thick silver (Ag) electrode, and the testing aperture area was 0.043 cm^2

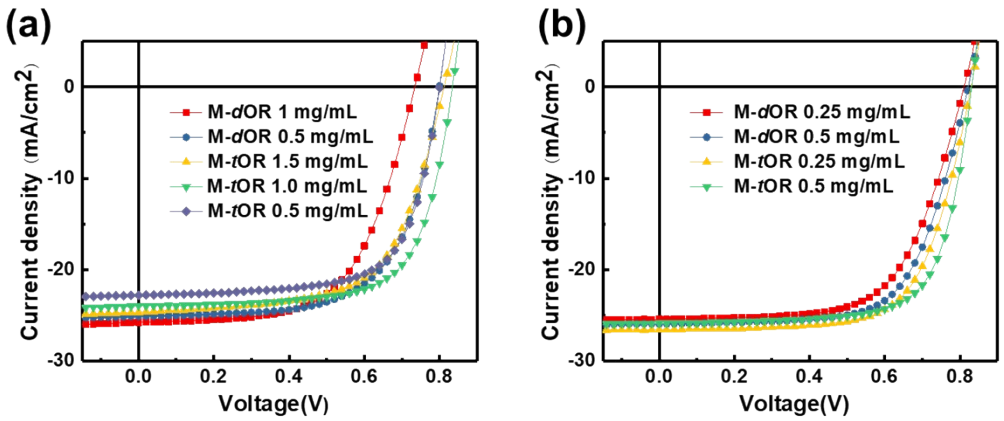

Figure S12. (a) *J-V* curve (CH_3OH solvent); (b) *J-V* curve (TFE solvent)

Table S1. Optimization parameters of CIL with different concentrations using CH_3OH as solvent

Spin speed/rpm	CIL	C（mg/mL）	[a]V_{OC} (V)	[a]J_{SC} (mA/cm^2)	[a]FF (%)	[a]PCE (%)
3000	**M-*d*OR**	1	0.73	25.78	60.37	11.42
		0.5	0.80	25.12	64.54	12.96
3000	**M-*t*OR**	0.5	0.80	22.81	68.59	12.52
3000		1	0.83	23.99	69.19	13.84
3000		1.5	0.81	24.67	62.84	12.59

Table S2. Optimization parameters of CIL with different concentrations using TFE as solvent

Spin speed/rpm	CIL	C（mg/mL）	[a]V_{OC} (V)	[a]J_{SC} (mA/cm^2)	[a]FF (%)	[a]PCE (%)
3000	**M-*d*OR**	0.25	0.82	25.94	66.05	14.09
3000		0.5	0.81	25.4	63.30	13.07
3000	**M-*t*OR**	0.25	0.83	25.88	71.42	15.36

3000		0.5	0.83	25.89	66.06	14.12

Table S3. Summary table of properties of several reported multi-arm CIL molecules based on different active layers

CIL	Active layer	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	Publish Date	Reference
OBN-Ph-N	PM6:L8-BO	0.87	26.65	73.60	17.06	2025.8.25	[1]
NTN	PM6:BTP-eC9	0.862	27.6	73.3	17.4	2025.2.26	[2]
NTRIC	PM6:BTP-eC9	0.825	28.3	73.3	17.1		[2]
BT-N-M	PM6:Y6	0.859	26.37	75.43	17.09	2025.8.17	[2]
3ONIN	PM6:BTP-eC9	0.827	27.58	73.74	16.73	2024.2.1	[2, 3]
NTA	PM6:Y6	0.849	26.72	74.3	16.86	2022.8.1	[4]
HPDIN-B01	PM6:BTP-BO-4Cl	0.848	26.65	76.77	17.40	2023.11.12	[5]
N-TBHOBM-*t*OR	PM6:Y6	0.843	26.33	75.64	16.78	2022.4.25	[6]
M-*t*OR	PM6:Y6	0.83	25.88	71.4	15.36	15.36	This Work

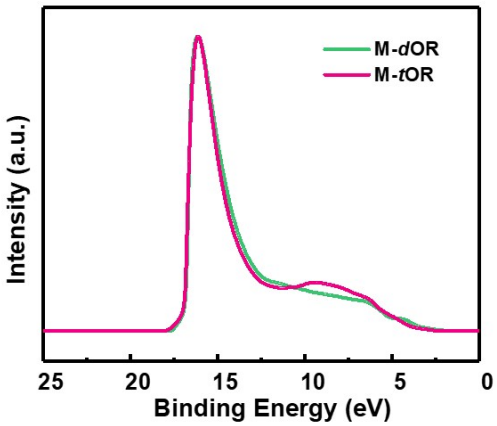

Figure S13. UPS spectra of **M-*d*OR**; and **M-*t*OR.**

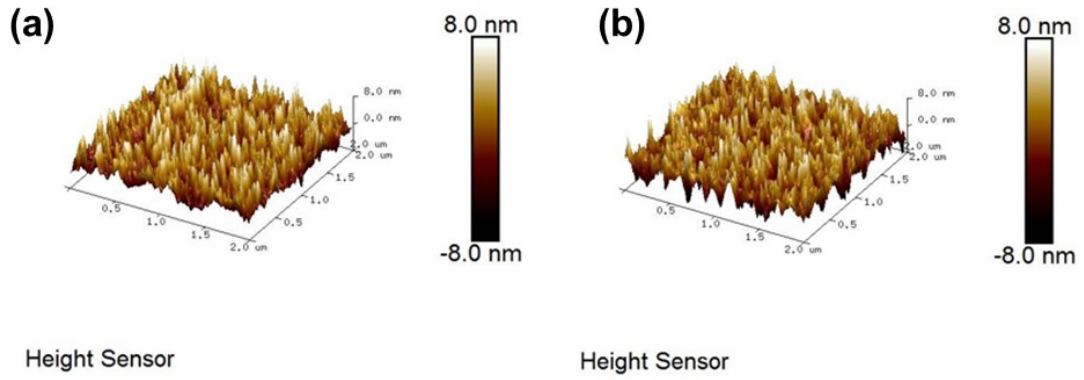

Figure S14. AFM 3D height image of **M-*d*OR**; and (b)**M-*t*OR.**

Reference:

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