

Supporting Information for

**Highly fluorescent triazolopyridine-thiophene D-A-D oligomers for
efficient pH sensing in both solution and solid state**

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yuyan19840218@hust.edu.cn

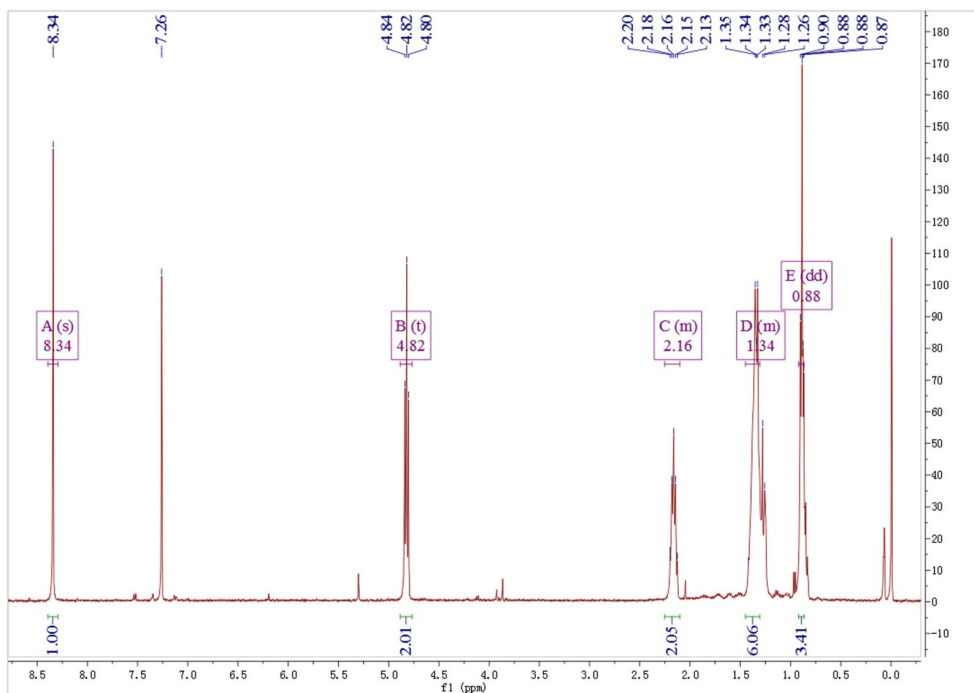


Fig. S1 ^1H NMR spectrum of 4,7-dibromo-hexyl[1,2,3]triazolo[4,5-c]pyridine (14a) in CDCl_3 .

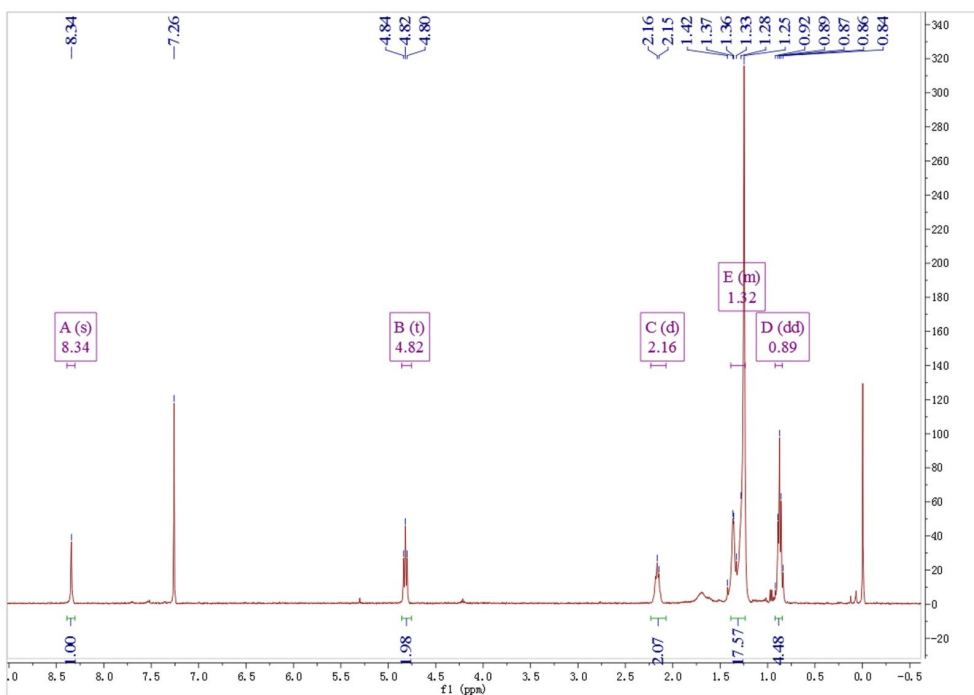


Fig. S2 ^1H NMR spectrum of 4,7-dibromo-dodecyl[1,2,3]triazolo[4,5-c]pyridine (14b) in CDCl_3 .

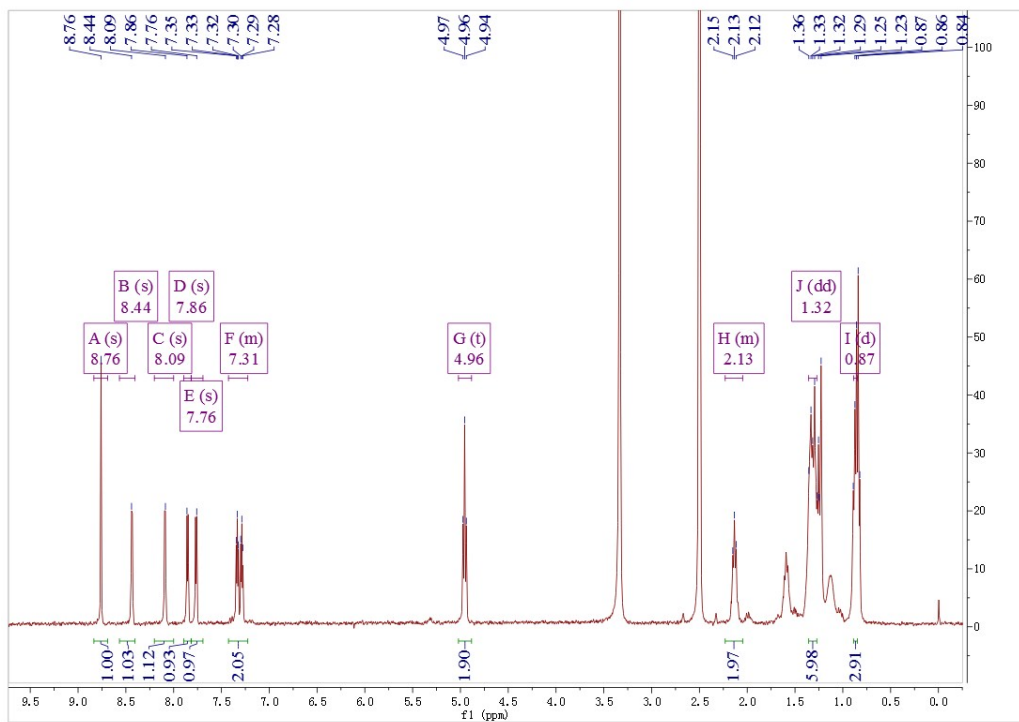


Fig. S3 ^1H NMR spectrum of Th-HPTz (**1**) in $\text{DMSO-}d_6$.

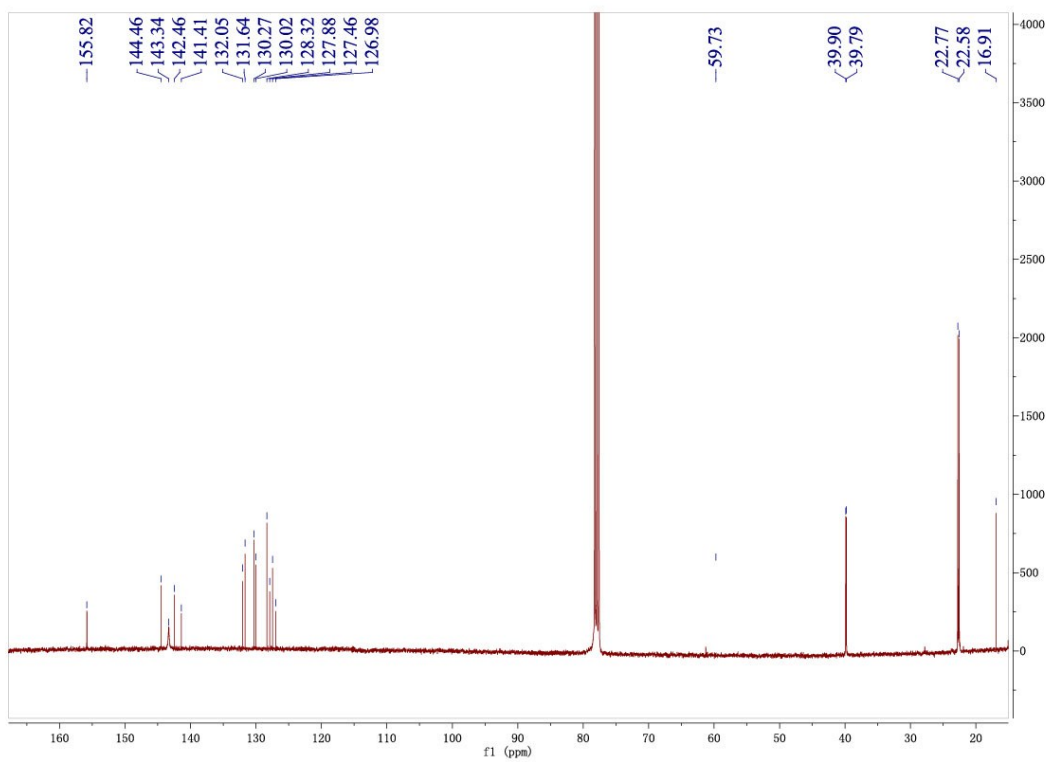


Fig. S4 ^{13}C NMR spectrum of Th-HPTz (**1**) in CDCl_3 .

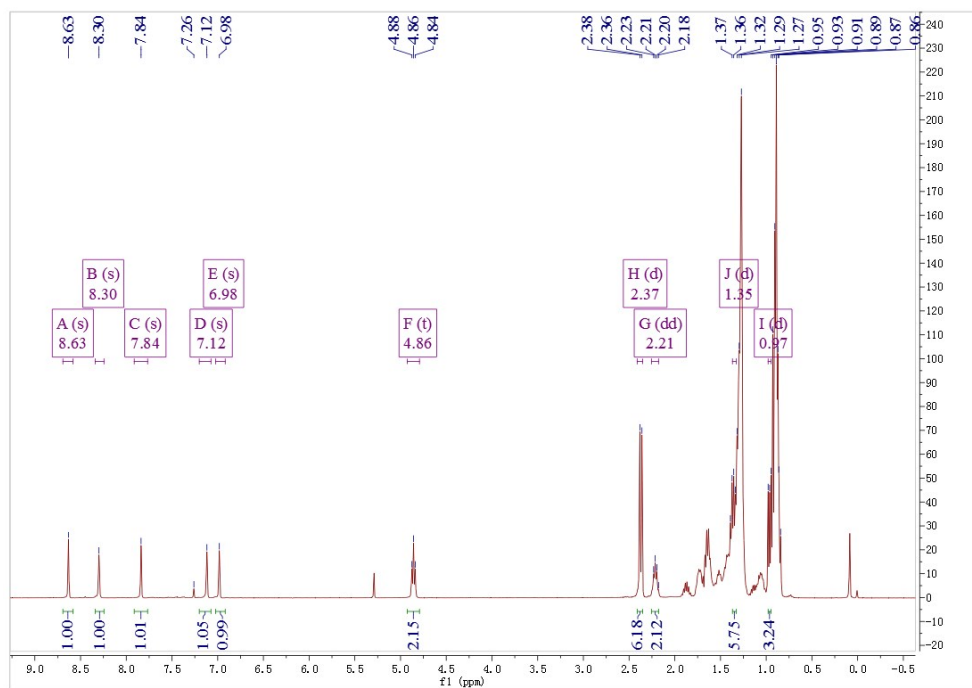


Fig. S5 ^1H NMR spectrum of 3MT-HPTz (**2**) in CDCl_3 .

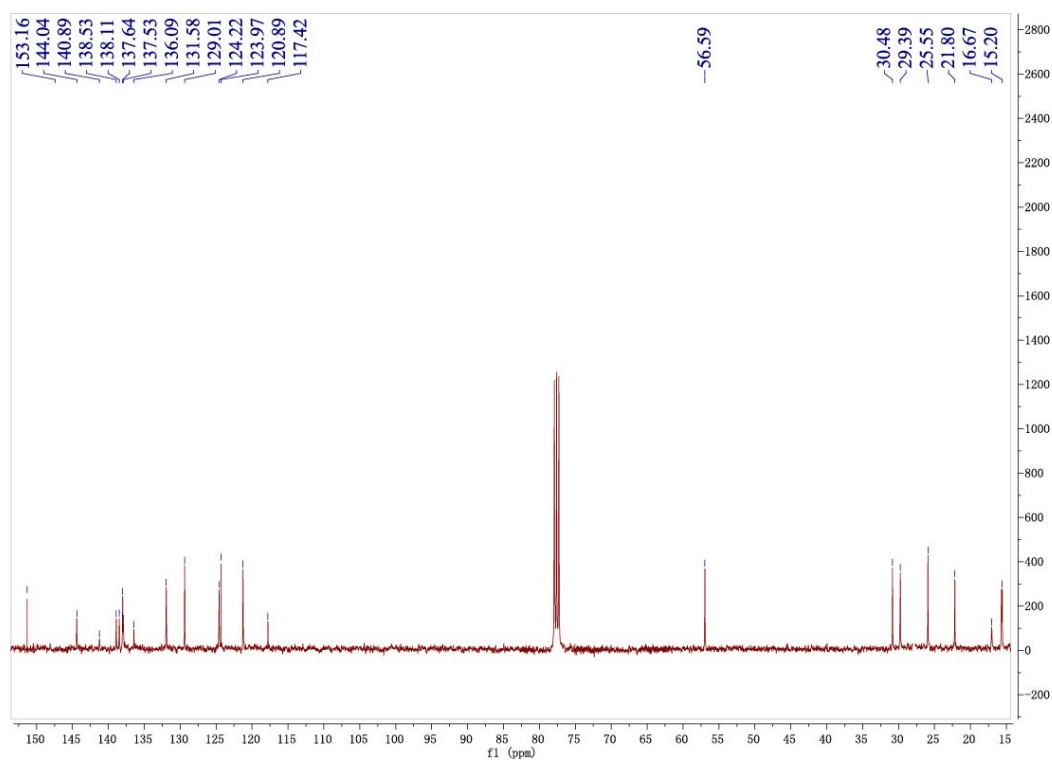


Fig. S6 ^{13}C NMR spectrum of 3MT-HPTz (**2**) in CDCl_3 .

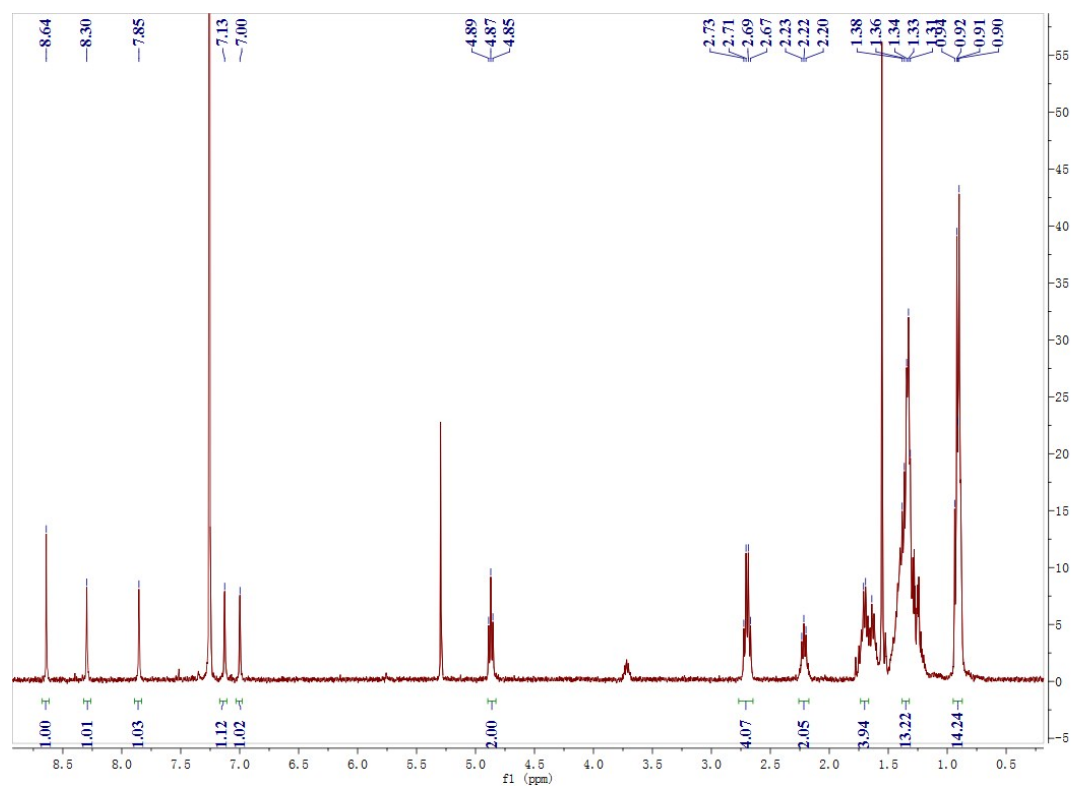


Fig. S7 ^1H NMR spectrum of 3HT-HPTz (**3**) in CDCl_3 .

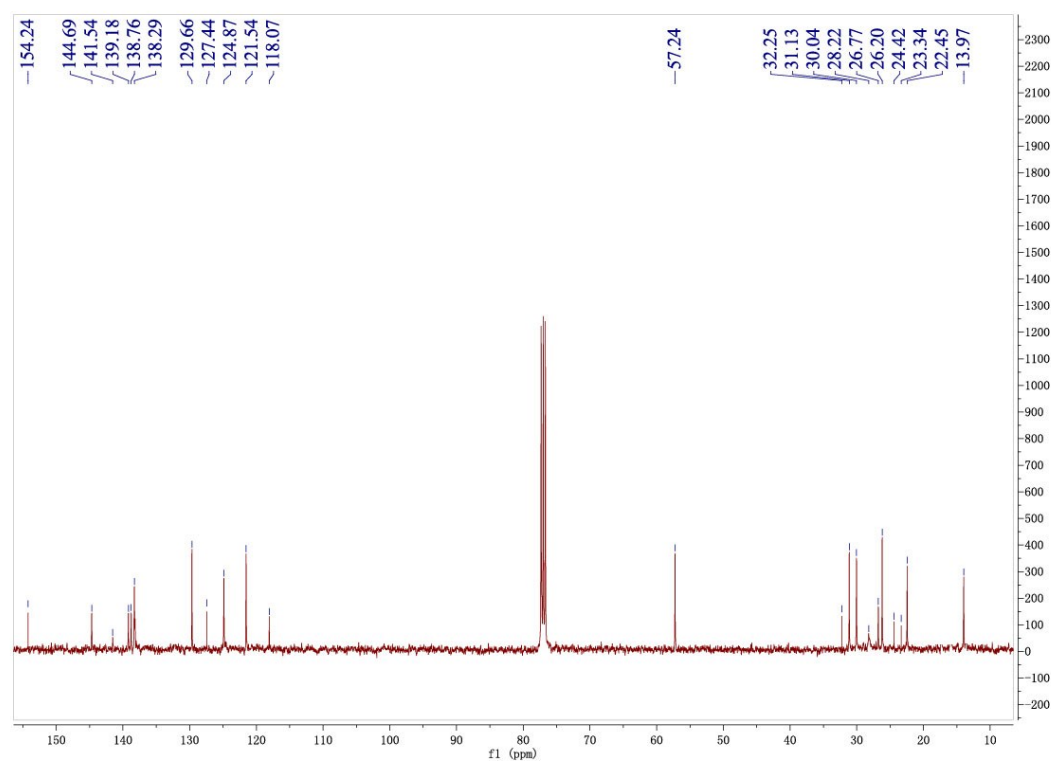


Fig. S8 ^{13}C NMR spectrum of 3HT-HPTz (**3**) in CDCl_3 .

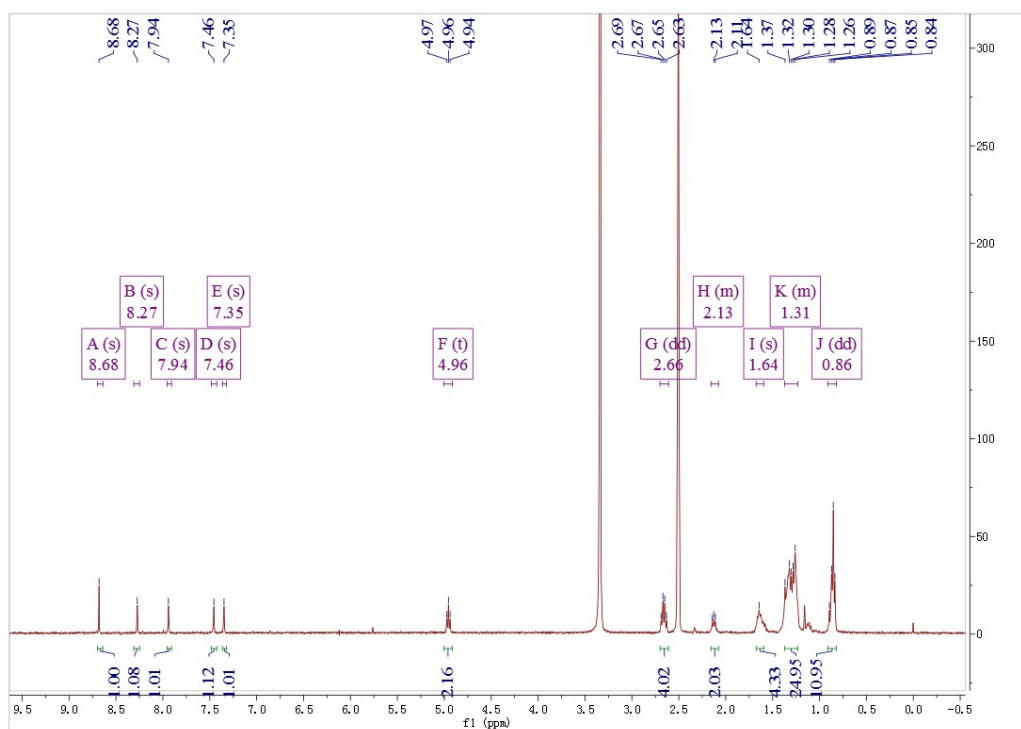


Fig. S9 ^1H NMR spectrum of 3OT-HPTz (**4**) in $\text{DMSO-}d_6$.

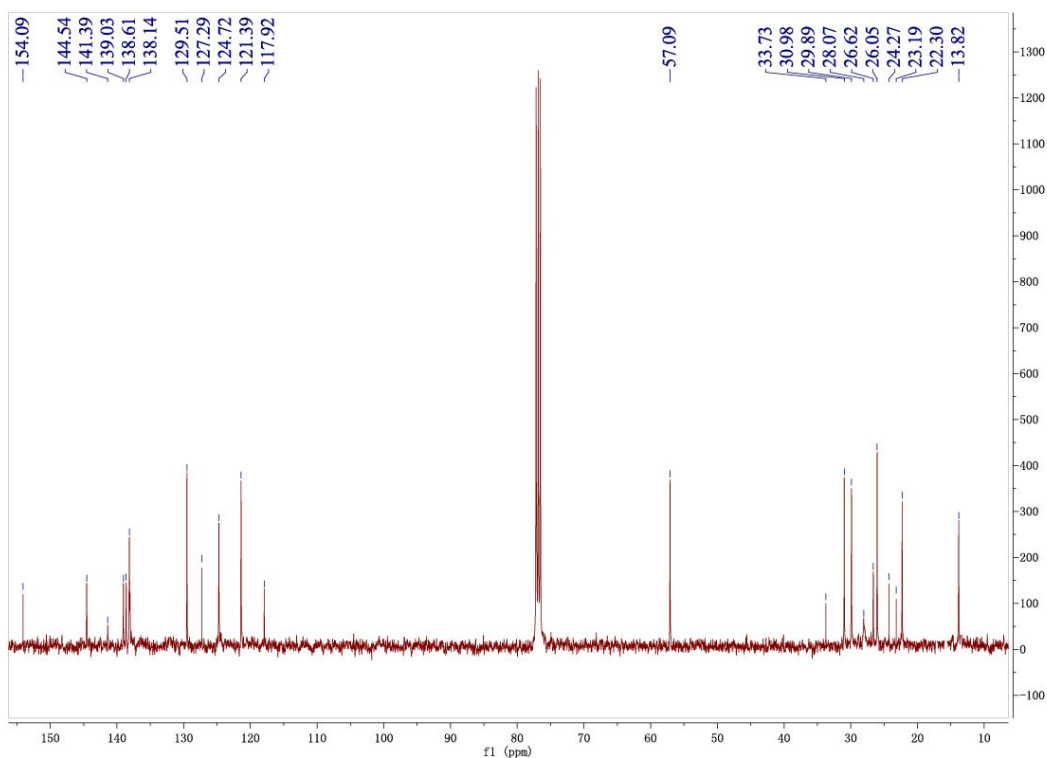


Fig. S10 ^{13}C NMR spectrum of 3OT-HPTz (**4**) in CDCl_3 .

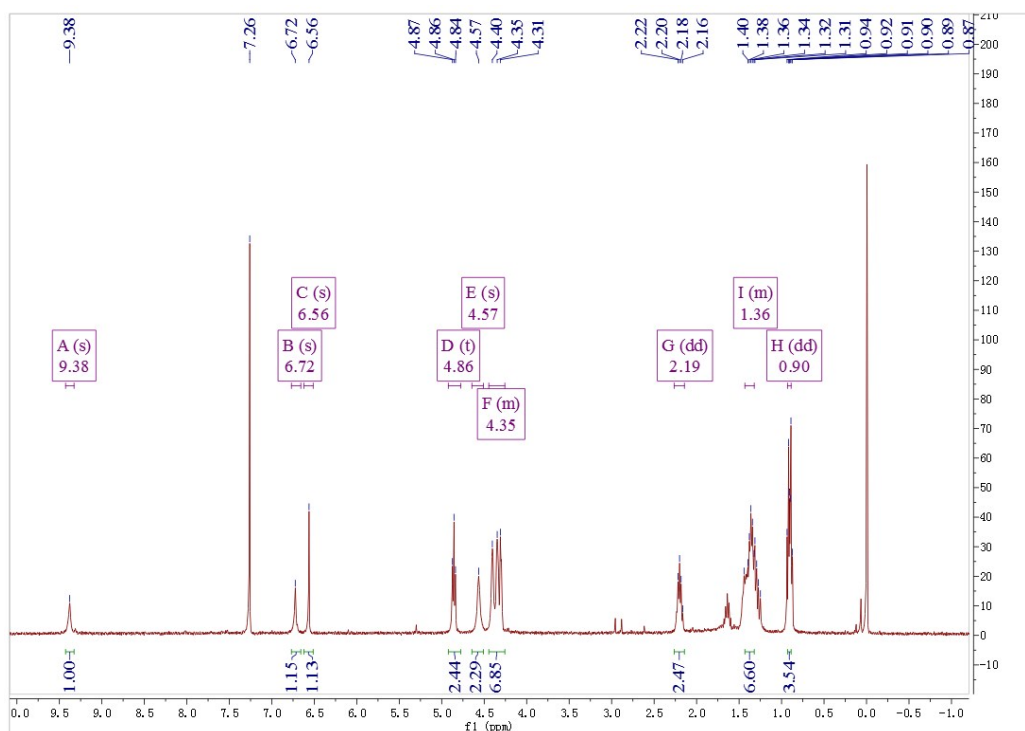


Fig. S11 ^1H NMR spectrum of EDOT-HPTz (**5**) in CDCl_3 .

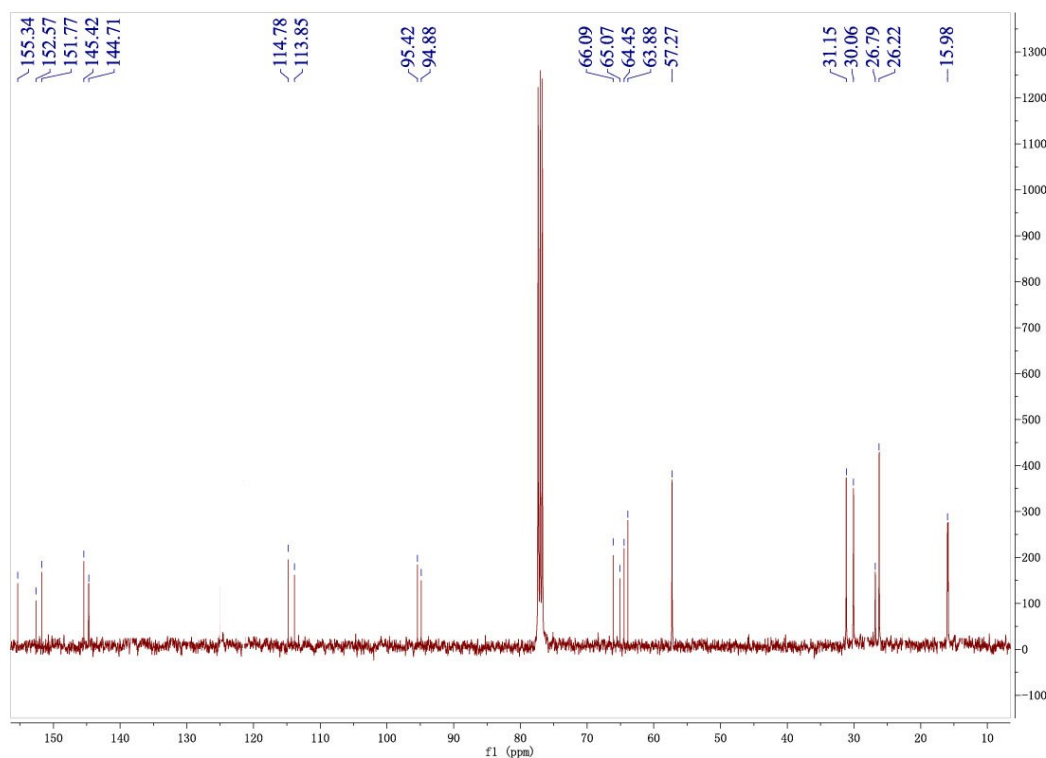


Fig. S12 ^{13}C NMR spectrum of EDOT-HPTz (**5**) in CDCl_3 .

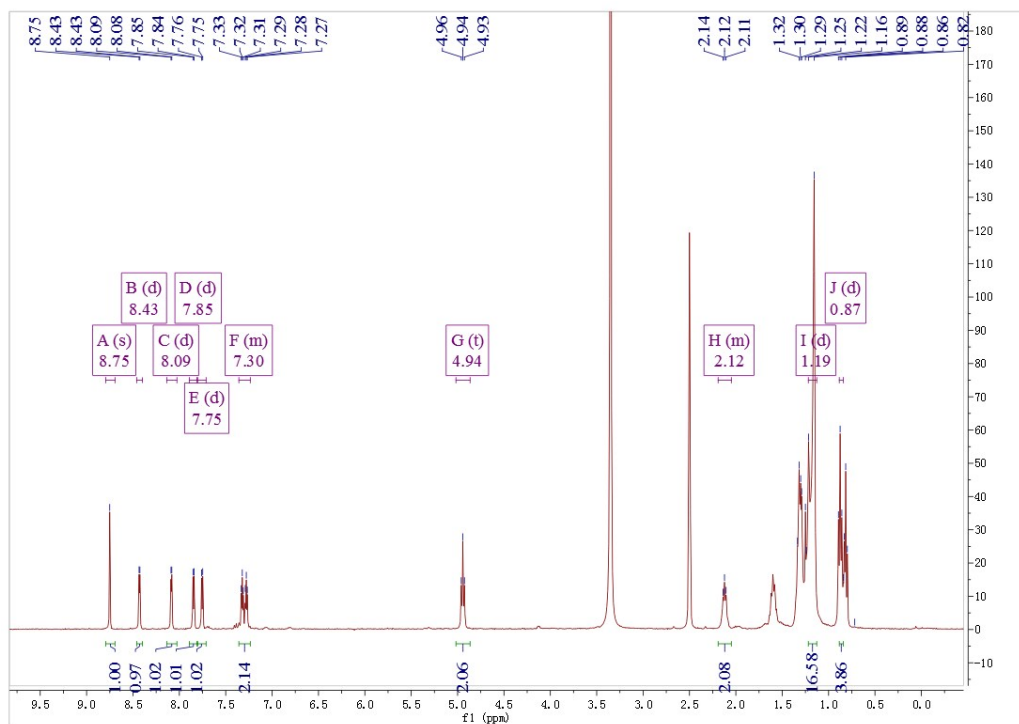


Fig. S13 ^1H NMR spectrum of Th-DPTz (**6**) in $\text{DMSO-}d_6$.

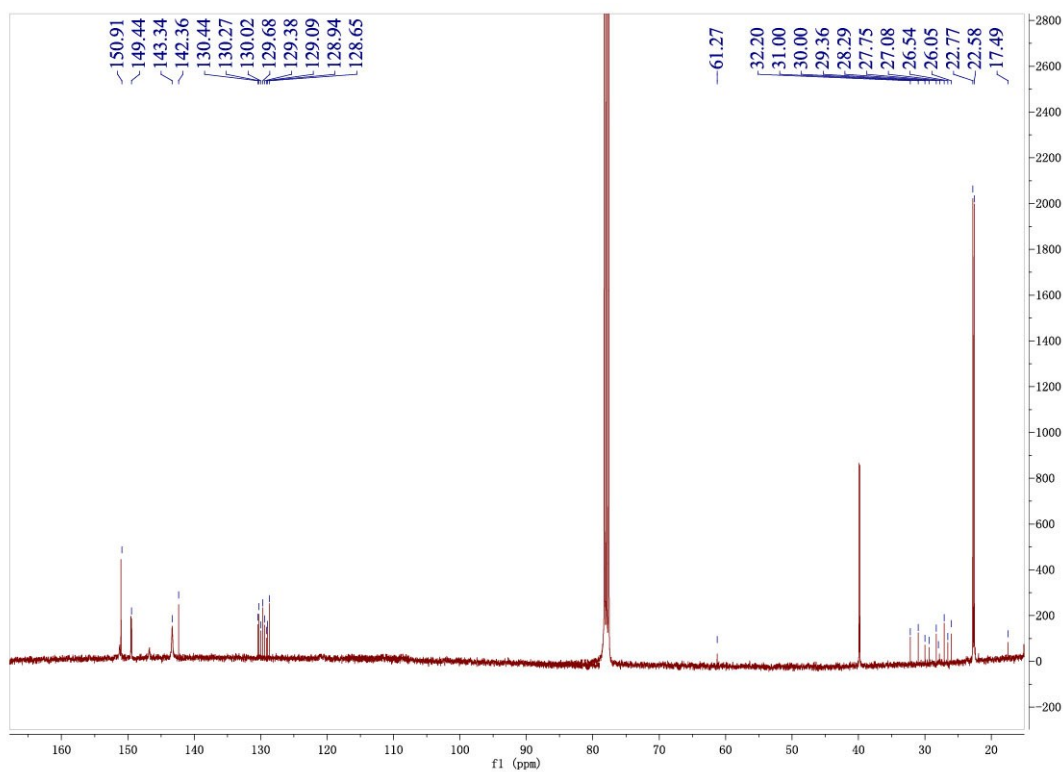


Fig. S14 ^{13}C NMR spectrum of Th-DPTz (**6**) in CDCl_3 .

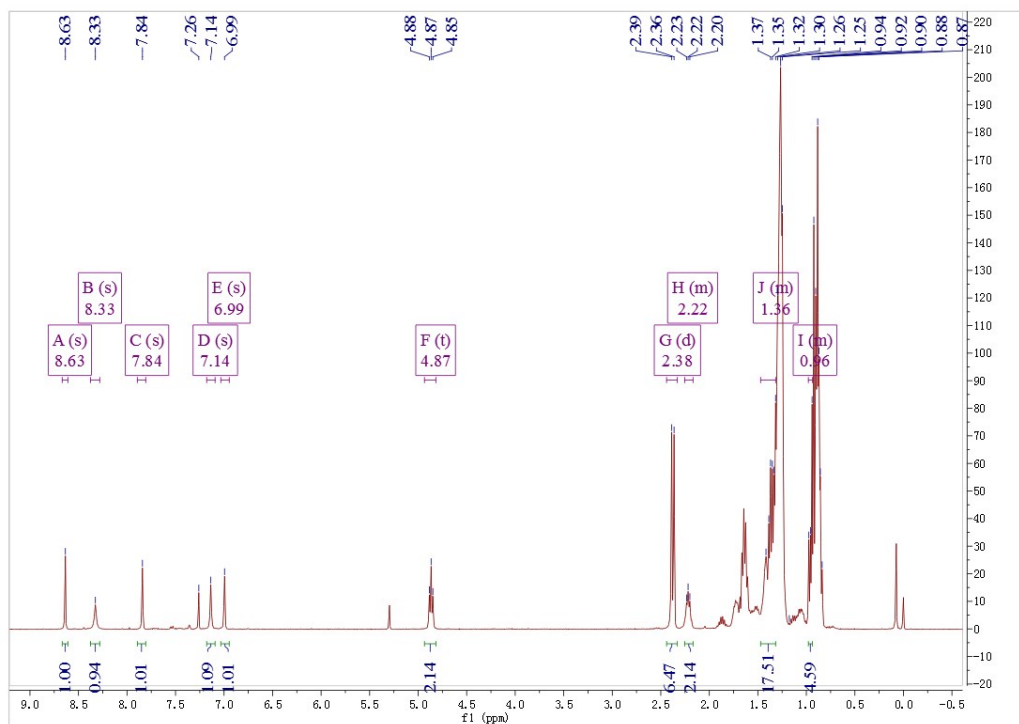


Fig. S15 ^1H NMR spectrum of 3MT-DPTz (**7**) in CDCl_3 .

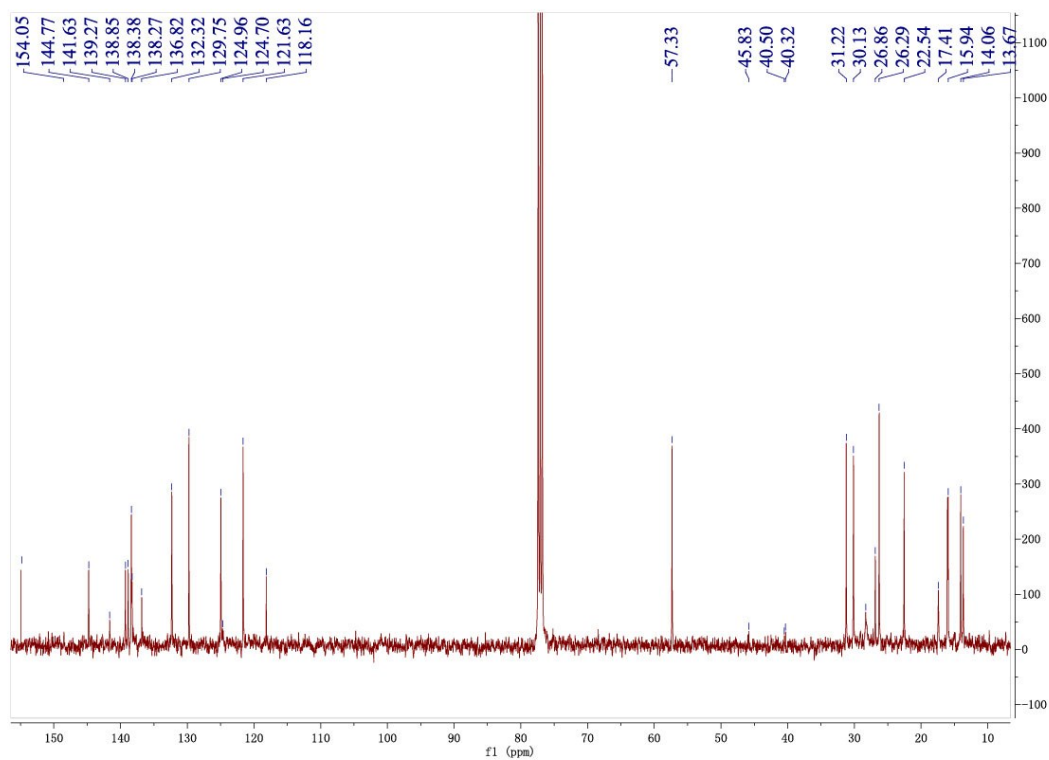


Fig. S16 ^{13}C NMR spectrum of 3MT-DPTz (**7**) in CDCl_3 .

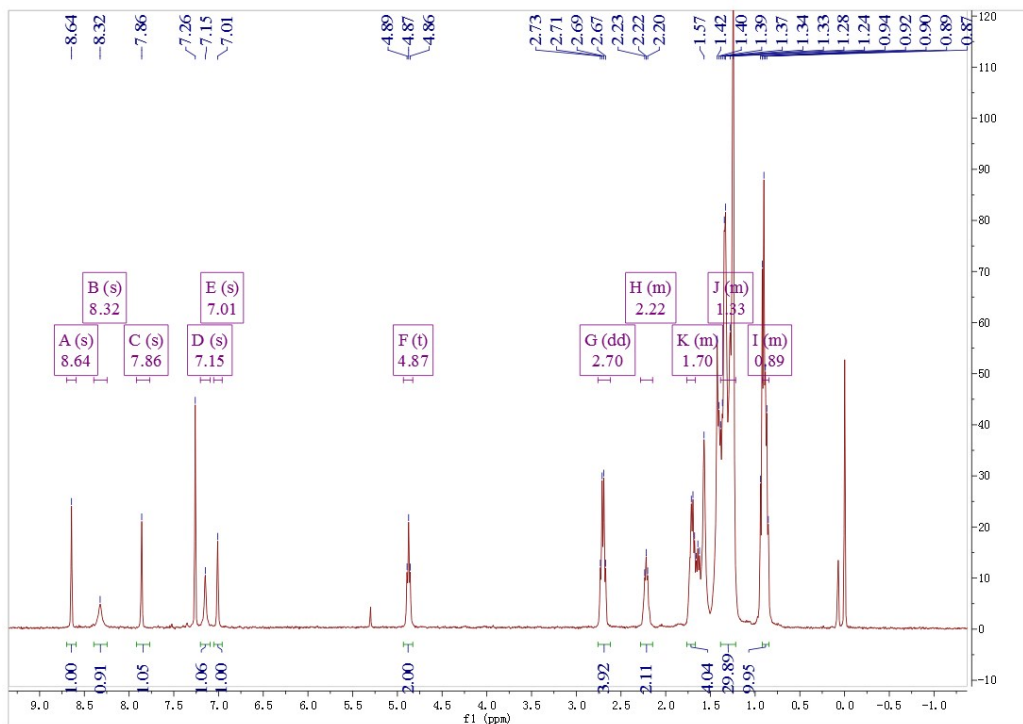


Fig. S17 ^1H NMR spectrum of 3HT-DPTz (**8**) in CDCl_3 .

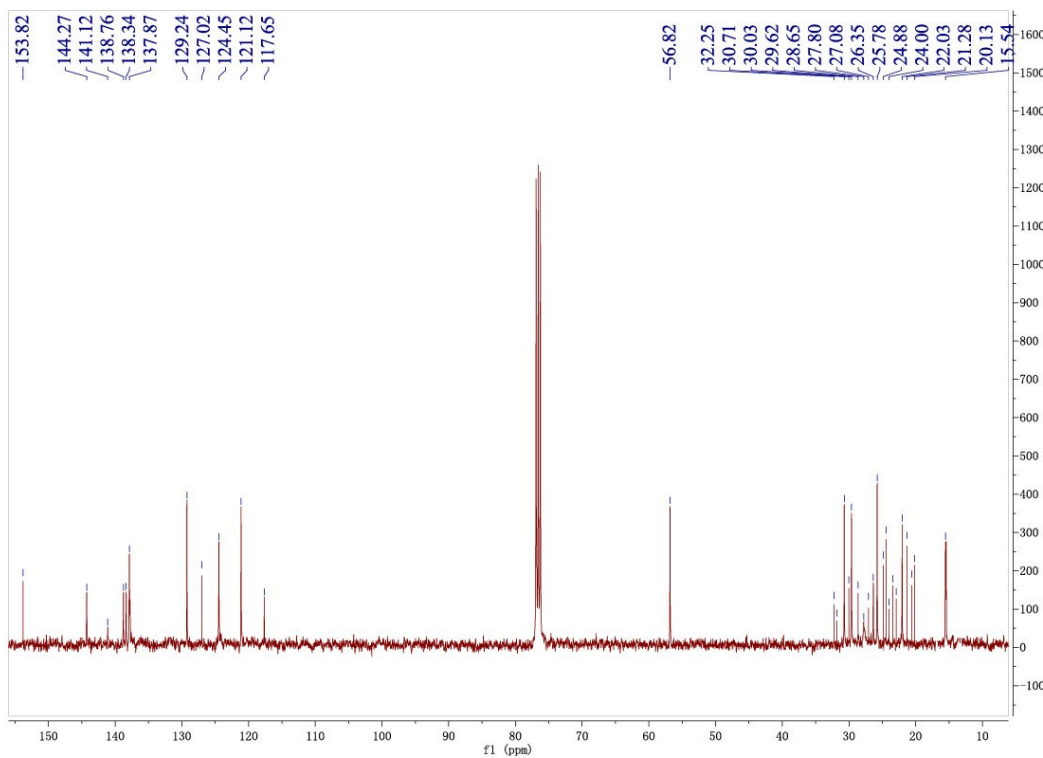


Fig. S18 ^{13}C NMR spectrum of 3HT-DPTz (**8**) in CDCl_3 .

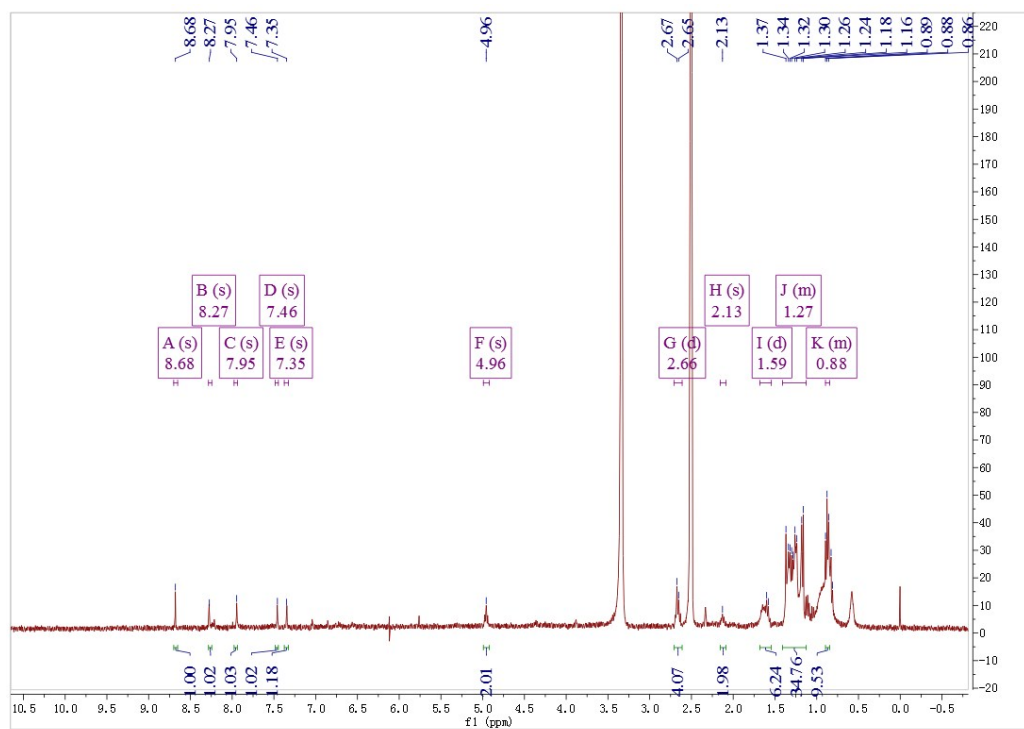


Fig. S19 ^1H NMR spectrum of 3OT-DPTz (**9**) in $\text{DMSO-}d_6$.

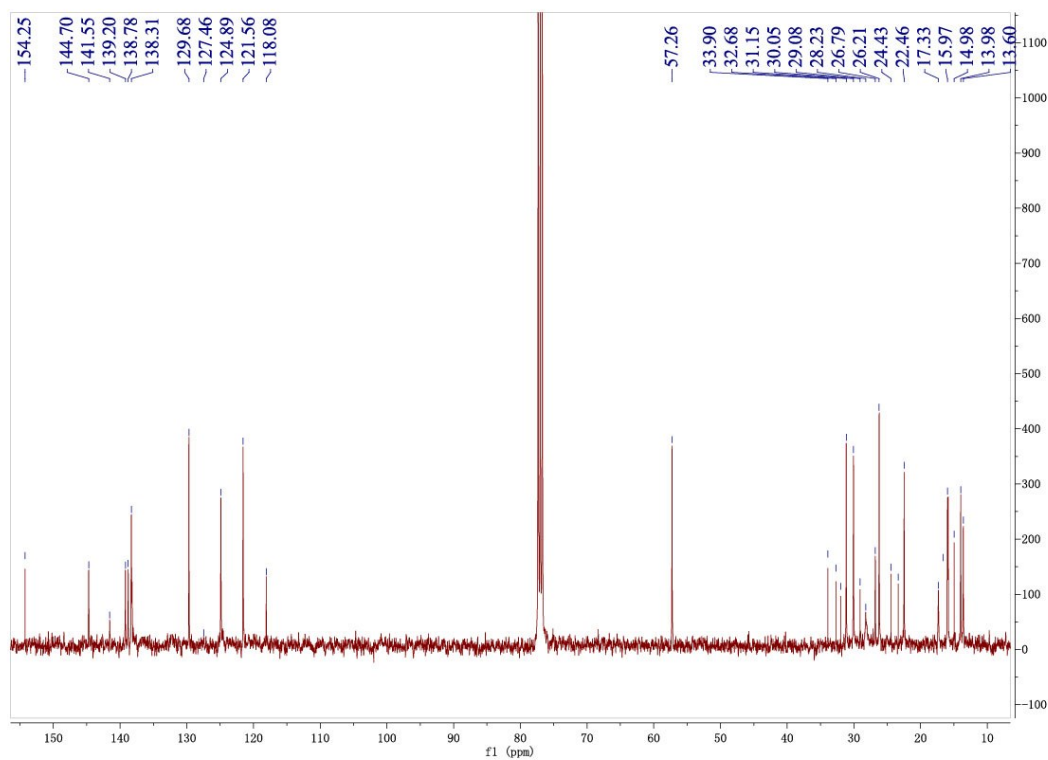


Fig. S20 ^{13}C NMR spectrum of 3OT-DPTz (**9**) in CDCl_3 .

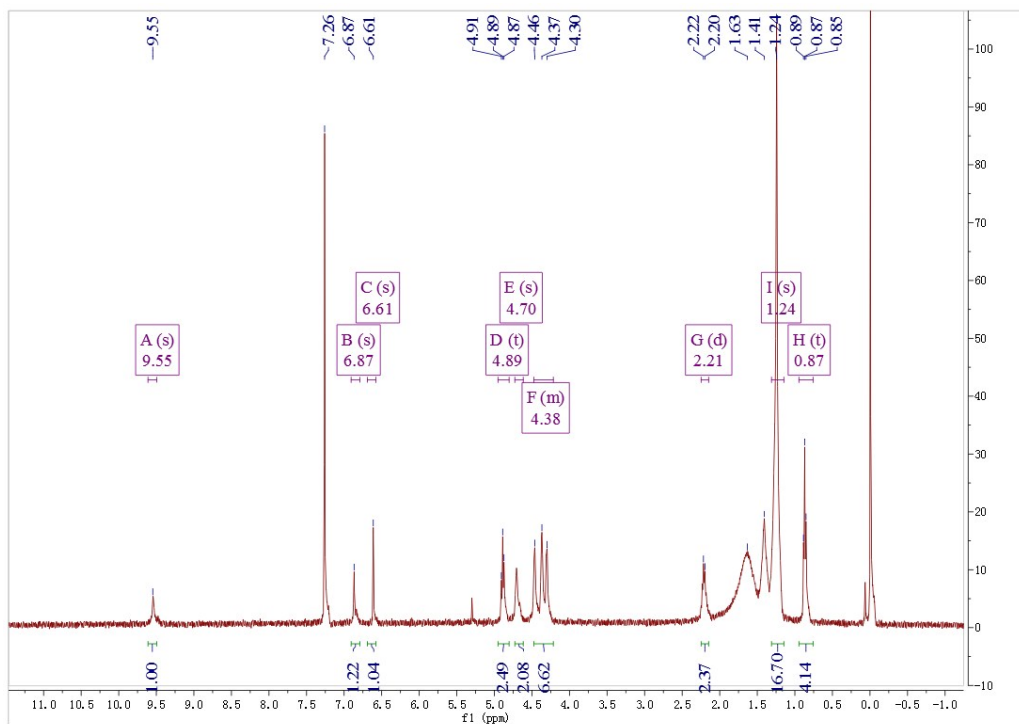


Fig. S21 ^1H NMR spectrum of EDOT-DPTz (**10**) in CDCl_3 .

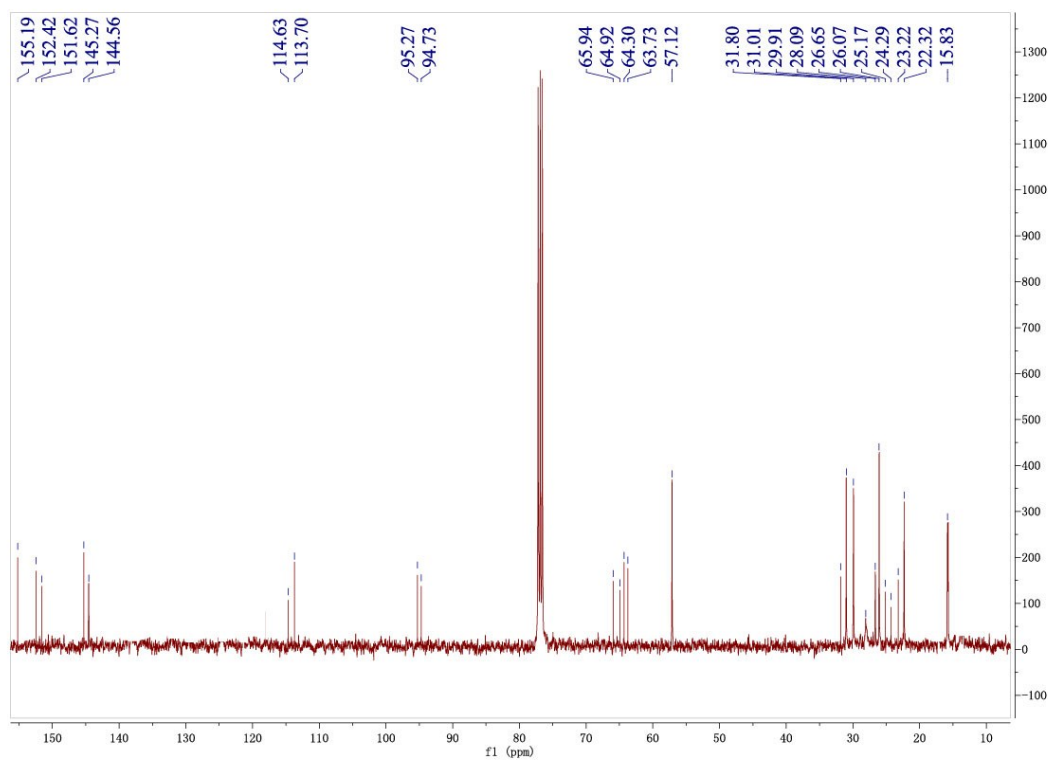


Fig. S22 ^{13}C NMR spectrum of EDOT-DPTz (**10**) in CDCl_3 .

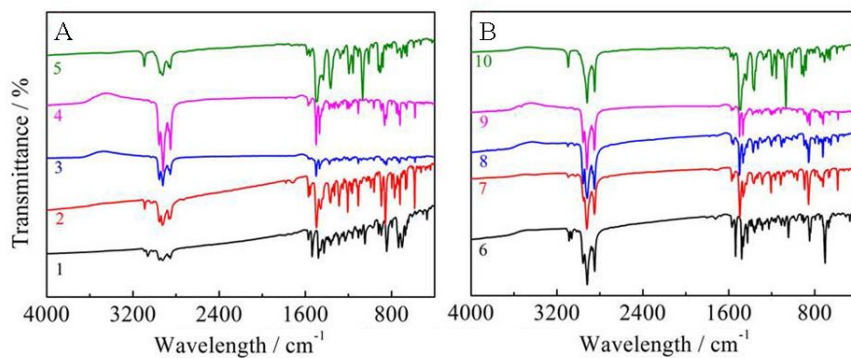


Fig. S23 FT-IR spectra of triazolopyridine-thiophene D-A-D type conjugated fluorophores (1~10).

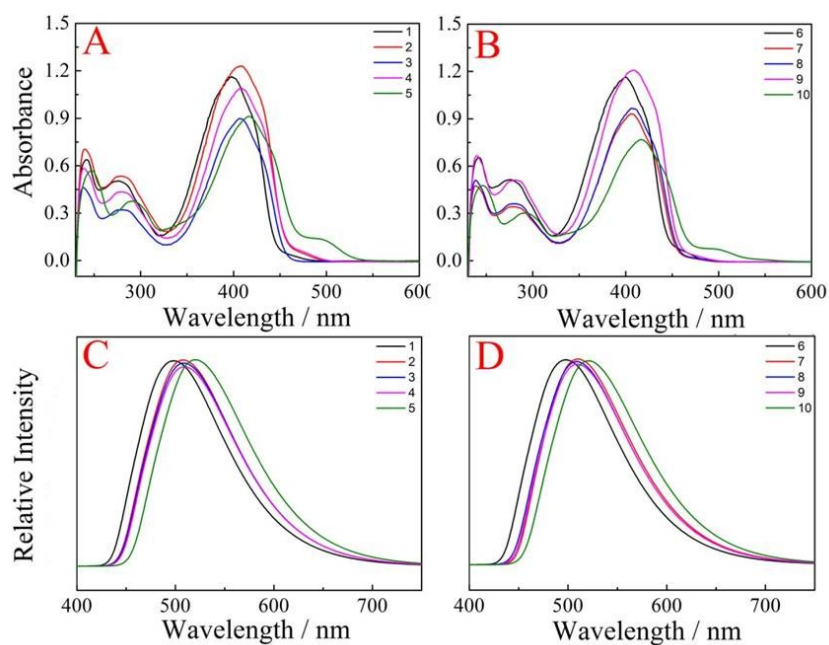


Fig. S24 UV-Vis absorption (A and B) and emission spectra (C and D) of triazolopyridine-thiophene D-A-D type conjugated fluorophores (1~10) in DCM.

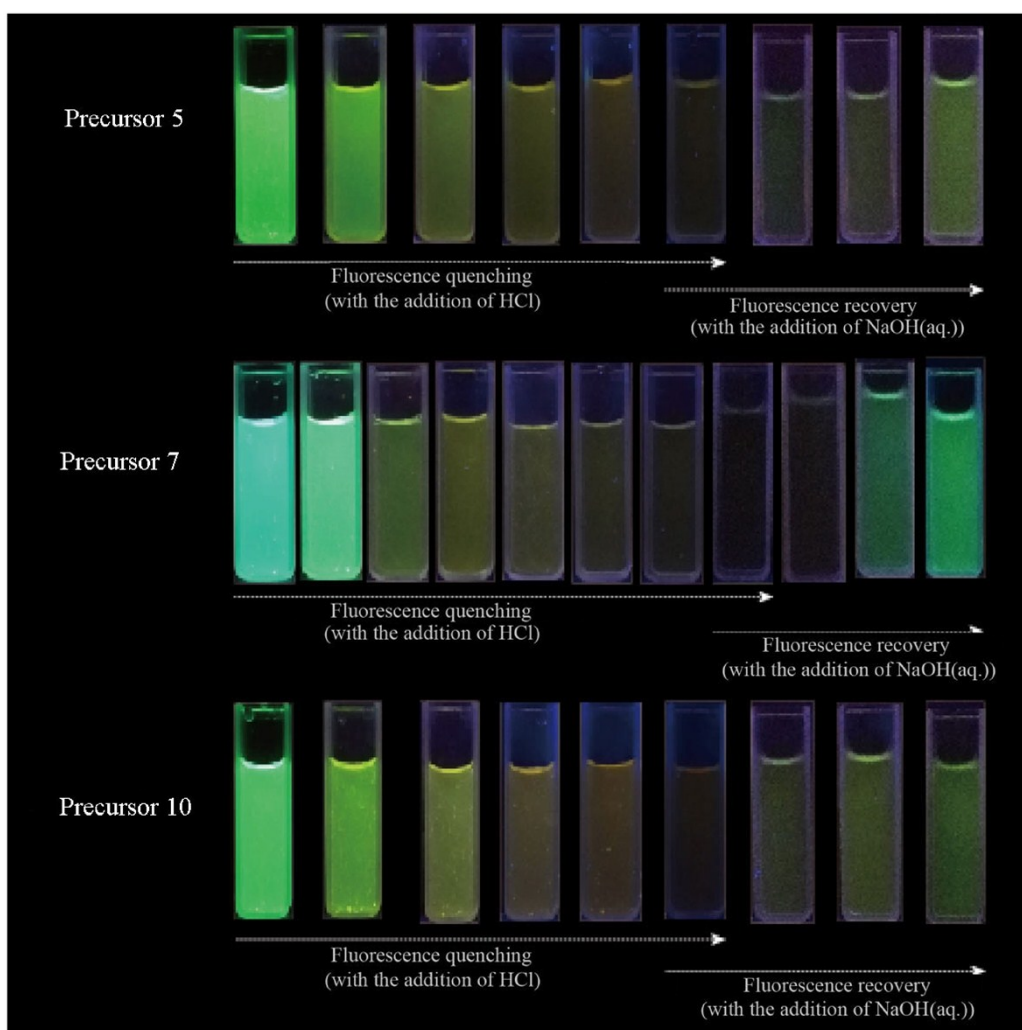


Fig. S25 Images of fluorescence quenching/recovery of triazolopyridine-thiophene D-A-D type conjugated fluorophores 5, 7 and 10 upon addition of HCl and reversed by NaOH in water-DMSO.

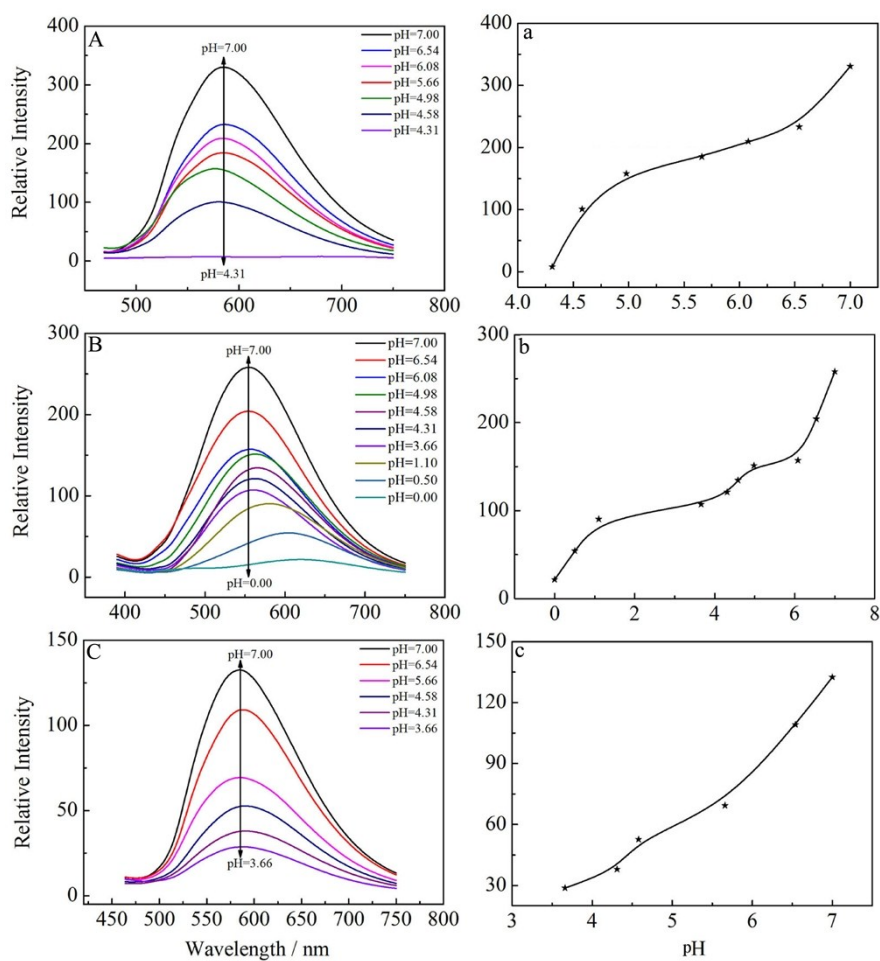


Fig. S26. (A-C) Fluorescence quenching in emission spectra of fluorophore 5, 7, and 10 (15 μM) by adding HCl. Excitation: 380 nm. (a-c) The corresponding calibration curve of I_{max} .

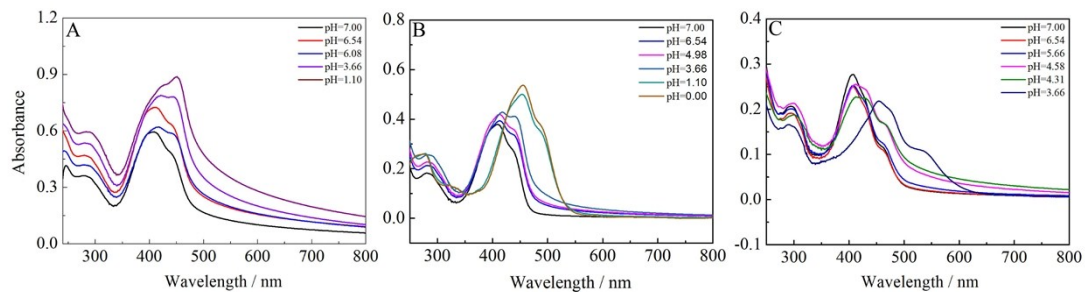


Fig. S27. The absorption spectral evolution of fluorophore 2 (A), 7 (B) and 10 (C) (15 μM).

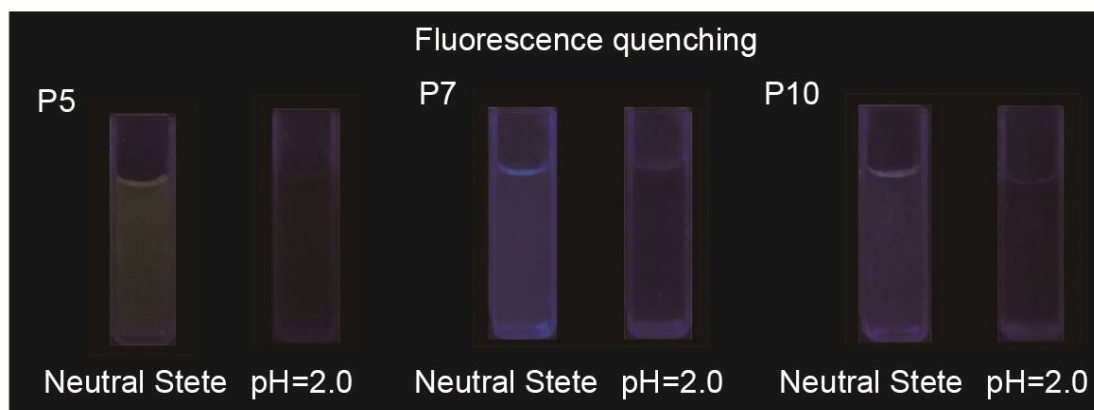


Fig. S28 Fluorescence quenching of P5, P7 and P10 (15 μ M in repeat units) at the neutral state and pH 2.0.

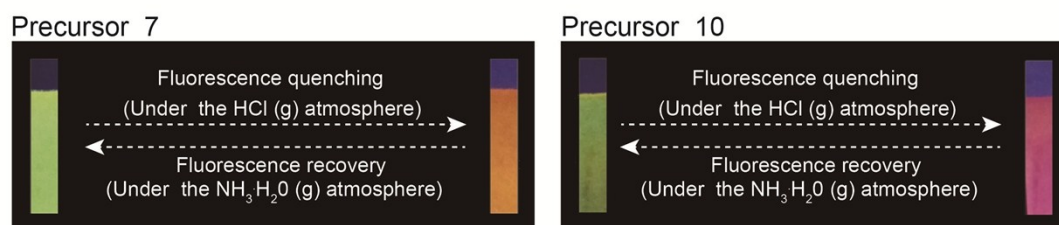


Fig. S29 The digital imaging of fluorophores 7/10-based fluorescence test papers in the both of HCl and NH₃·H₂O vapor.

Table S1 Peak assignments and comparison between observed peaks of triazolopyridine-thiophene D-A-D type conjugated fluorophores (1~10).

Peak(cm ⁻¹) 1/2/3/4/5/6/7/8/9/10	Assignment
3085/ 3087/ 3080/ 3091/ 3088/ 3092/ 3088/ 3087/ 3089/ 3087	=C-H vibration of thiophene
2831, 2847/ 2927, 2853/ 2934, 2854/ 2930, 2849/ 2926, 2852/ 2820, 2846/ 2934, 2825/ 2921, 2845/ 2922, 2848/ 2929, 2850	=C-H vibration of pyridine or triazole
1587, 1550/ 1579, 1552/ 1581, 1549/ 1582, 1547/ 1580, 1548/ 1581, 1550/ 1580, 1557/ 1584, 1557/ 1585, 1552/ 1579, 1549	ring vibration of substituted pyridine
1491/ 1489/ 1493/ 1492/ 1495/ 1491/ 1493/ 1492/ 1492/ 1490	C=C vibration of pyridine or C=N vibration of triazole
1362/ 1365/ 1368/ 1360/ 1364/ 1369/ 1368/ 1367/ 1362/ 1360	ring vibration of substituted thiophene
1201, 1150/ 1195, 1151/ 1221, 1154/ 1204, 1150/ 1197, 1155/ 1195, 1147/ 1195, 1153/ 1195, 1158/ 1197, 1159/ 1198, 1152	=C-H in-plane of thiophene
1071/ 1072/ 1058/ 1056/ 1070/ 1067/ 1062/ 1059/ 1057/ 1069	=C-H out-of-plane of pyridine or triazole
711/ 713/ 698/ 697/ 701/ 705/ 695/ 691/ 701/ 703	=C-H out-of-plane of thiophene

Table S2 DFT calculated molecular geometries and frontier molecular orbital distributions for the model structures.

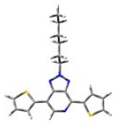
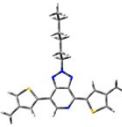
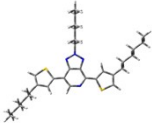
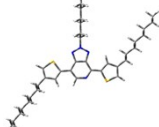
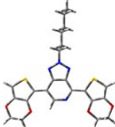
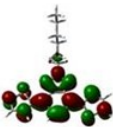
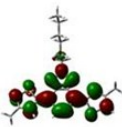
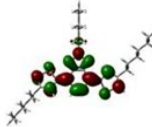
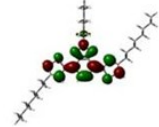
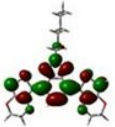
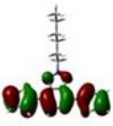
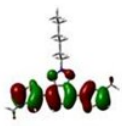
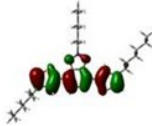
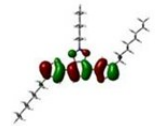
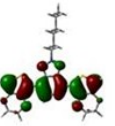
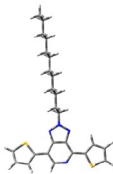
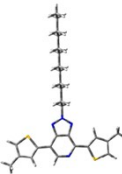
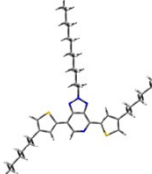
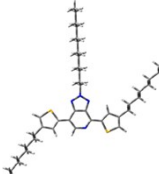
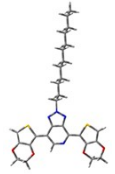
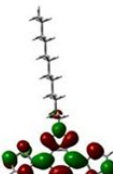
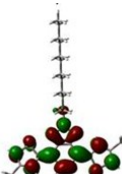
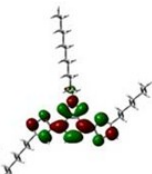
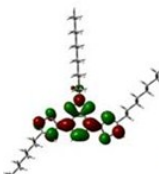
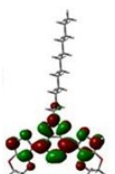
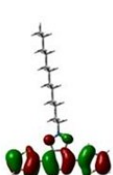
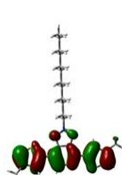
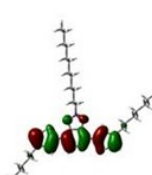
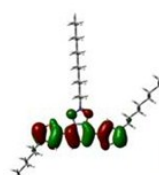
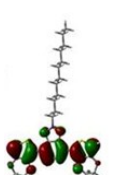
Monomers	1	2	3	4	5
Optimized geometry					
LUMO					
HOMO					
Monomers	6	7	8	9	10
Optimized geometry					
LUMO					
HOMO					

Table S3 Optical parameters and DFT theoretical calculation data of previously reported chalcogenodiazolo[3,4-c]pyridine-based molecular systems.

Precursors	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{onset} (nm)	$E_{\text{g,opt}}$ (eV)	$\lambda_{\text{max,1}}$ (nm)	$\lambda_{\text{max,2}}$ (nm)	$\lambda_{\text{max,3}}$ (nm)	λ_{em} (nm)	ϕ_{F}	Ref.
ProDOT(Me) ₂ -PT	-5.93	-3.88	563	2.20	263	309	481	661	0.602	[23]
ProDOT(Me) ₂ -PSe	-5.86	-4.16	604	2.05	268	321	518	673	0.137	[23]
ProDOT(Bu) ₂ -PT	-5.81	-3.97	565	2.19	264	311	485	721	0.477	[23]
ProDOT(Bu) ₂ -PSe	-5.77	-3.97	702	1.77	270	325	526	715	0.088	[23]
EDOT-PT	-5.68	-3.54	579	2.14	266	315	500	653	0.501	[22,25]
EDOT-PSe	-5.61	-3.67	639	1.94	274	328	542	714	0.072	[25]
HexTh-PT	-5.95	-3.71	554	2.24	255	307	479	618	0.711	[25]
HexTh-PSe	-5.85	-3.80	605	2.05	252	317	515	648	0.184	[25]
MeTh-PT	-5.81	-3.56	551	2.25	256	305	476	615	0.701	[25]
MeTh-PTSe	-5.80	-3.74	602	2.06	253	316	502	613	0.200	[25]
Th-PT	-6.04	-3.73	537	2.31	258	302	464	603	0.849	[25]
Th-PSe	-5.90	-3.59	582	2.13	270	313	498	643	0.307	[25]