Supporting Information for

Quinoidal π-extension of dipyranylidene derivatives: towards efficient dopants for n-type organic semiconductors

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Contents

1. Estimation of E_{HOMO}s of DP8 and DP9 by theoretical calculations

Table S1. Calculated E_{HOMO}s of DP0, DP7, DP8, and DP9. [1]

Compounds	E_{HOMO} / eV [a]
DP0	–4.31
DP7	–3.56
DP8	–3.94
DP9	–3.29

[a] Calculated with the DFT method at the B3LYP / 6-311G* level.

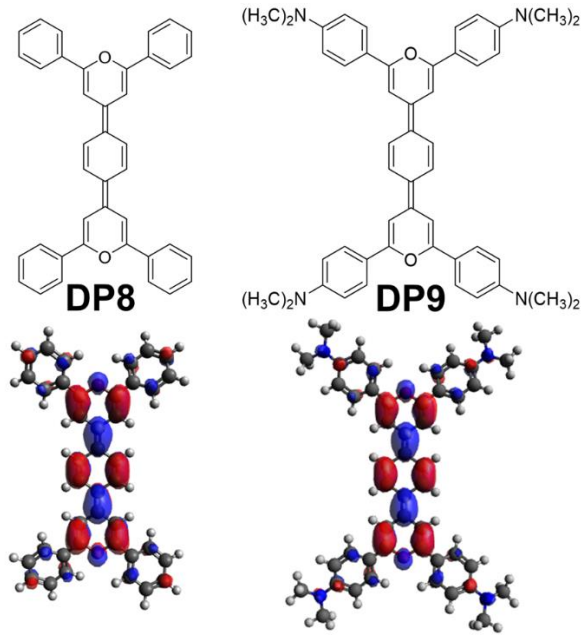

Fig. S1. HOMOs of DP8 and DP9.

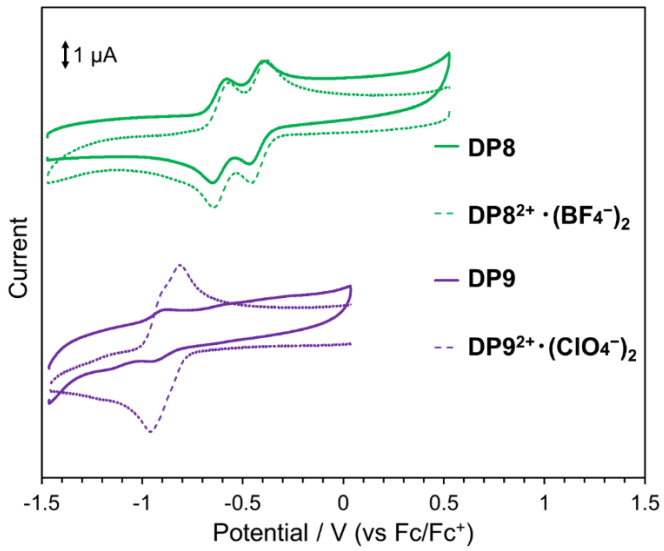

Fig. S2. Cyclic voltammograms of $DP8^{2+}\cdot(BF_4^-)_2$/DP8 (superimposed) and $DP9^{2+}\cdot(ClO_4^-)_2$/DP9 (superimposed).

2. Single-crystal X-ray analysis of DP8 and DP9

Table S2. Crystallographic data of DP8 and DP9.

Formula	$C_{40}H_{28}O_2$	$C_{48}H_{48}N_4O_2$
Formula weight	540.62	712.94
Temperature / K	293 (2)	100 (2)
Crystal habit	Plate	Needle
Crystal system	*Monoclinic*	*Monoclinic*
Space group	*I2/a*	$P2_1/n$
a / Å	17.0901(7)	6.3854(1)
b / Å	5.7243(2)	7.7628(1)
c / Å	29.7971(11)	37.5449(5)
β / °	104	90.494(1)
V / Å3	2827.04(19)	1860.98(5)
Z	4	2
R, Rw	0.0619, 0.1403	0.0499, 0.1386
GOF	1.053	1.034
Compound	DP8	DP9

3. Evaluation of thermoelectric properties

3.1. Methods [2]

Glass substrates were ultrasonicated in water for 3 min thrice and in acetone for 10 min, rinsed in boiling isopropanol, and then subjected to UV-ozone treatment for 30 min. Then, a pair of gold electrodes (thickness: 100 nm) (gap/width (G/W) = 0.1/1.5 mm for conductivity measurements or 0.5/8.5 mm for Seebeck coefficient measurements) were deposited on top of the glass substrates.

Two-terminal conductivity measurement was carried out inside a nitrogen-filled glovebox with a Keithley 4200-SCS semiconductor parameter analyzer. The conductivities reported in this work were obtained by averaging more than 5 devices. The thickness of the thin films was measured on a surface profiler AMBIOS TECHNOLOGY XP-100. Seebeck coefficients were measured in a nitrogen-filled glovebox with a Keithley 2182A nanovoltmeter. The temperature difference ($\Delta T \leqq 2$ K) across the sample was applied with two Peltier modules, and the thermovoltage (ΔV) was measured between the two electrodes. The Seebeck coefficients reported in this chapter were obtained by averaging 2 devices.

3.2. BBL

A solution of BBL in methanesulfonic acid (7.5 g L^{-1}) was stirred at 70 °C for 2 h. The solution was spin-coated on the glass substrates at 2000 rpm for 30 sec. The BBL thin-films were dipped immediately into deionized water to remove residual methanesulfonic acid. The obtained BBL thin-films were dried first on a hot plate at 100 °C in ambient conditions, then thermally annealed on a hot plate at 200 °C in a nitrogen-filled glovebox for 1 h, and were cooled down to room temperature. The BBL thin-films were doped with the chloroform solution of DP8 (1.0 g L^{-1}), DP9 (1.0 g L^{-1}), and *N*-DMBI (10 g L^{-1}) by placing the solution on top of the pristine BBL-thin-films, waiting 5 seconds,

and then spinning the excess solutions off at 1000 rpm.

3.3. N2200

Chloroform solutions of N2200 (2.5 ~ 10 g L^{-1}), DP9 (1.0 g L^{-1}) and *N*-DMBI (0.42 ~ 1.1 g L^{-1}) were prepared separately. Aliquots of dopants and polymer solutions were mixed at room temperature to reach a concentration of N2200 (2 g L^{-1}) with DP9, and (5 g L^{-1}) with *N*-DMBI, and then stirring for 15 min. The solution of N2200-DP2 was spin-coated on glass substrates at 200 rpm for 120 sec and the solution of N2200-*N*-DMBI was spin-coated on glass substrates at 1000 rpm for 35 sec, and the resulting thin films on the substrates were annealed at 150 °C for 15 min and allowed to cool to room temperature.

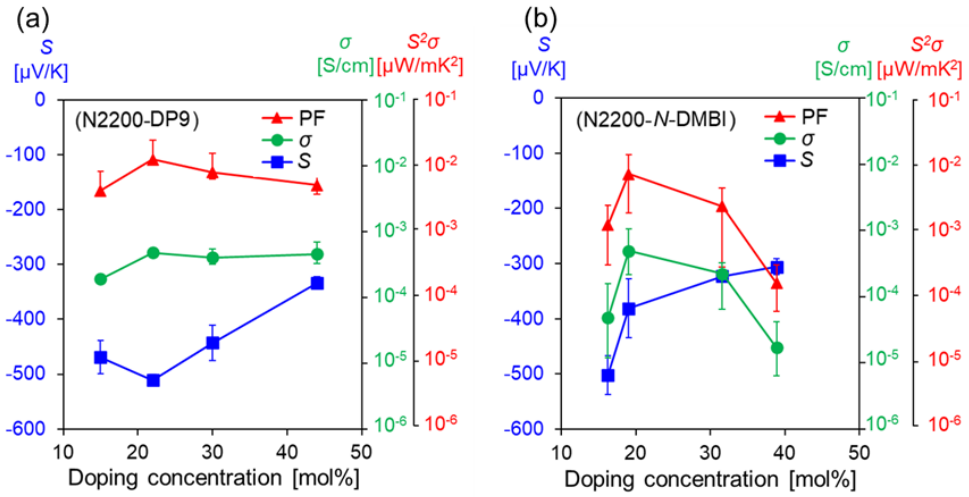

Fig. S3. Properties of doped N2200 thin films doped with DP9 (a), and *N*-DMBI (b) depending on the doping concentration.

4. NMR spectra of $DP8^{2+}\cdot(BF_4^-)_2$, DP8, 2, and $DP9^{2+}\cdot(ClO_4^-)_2$

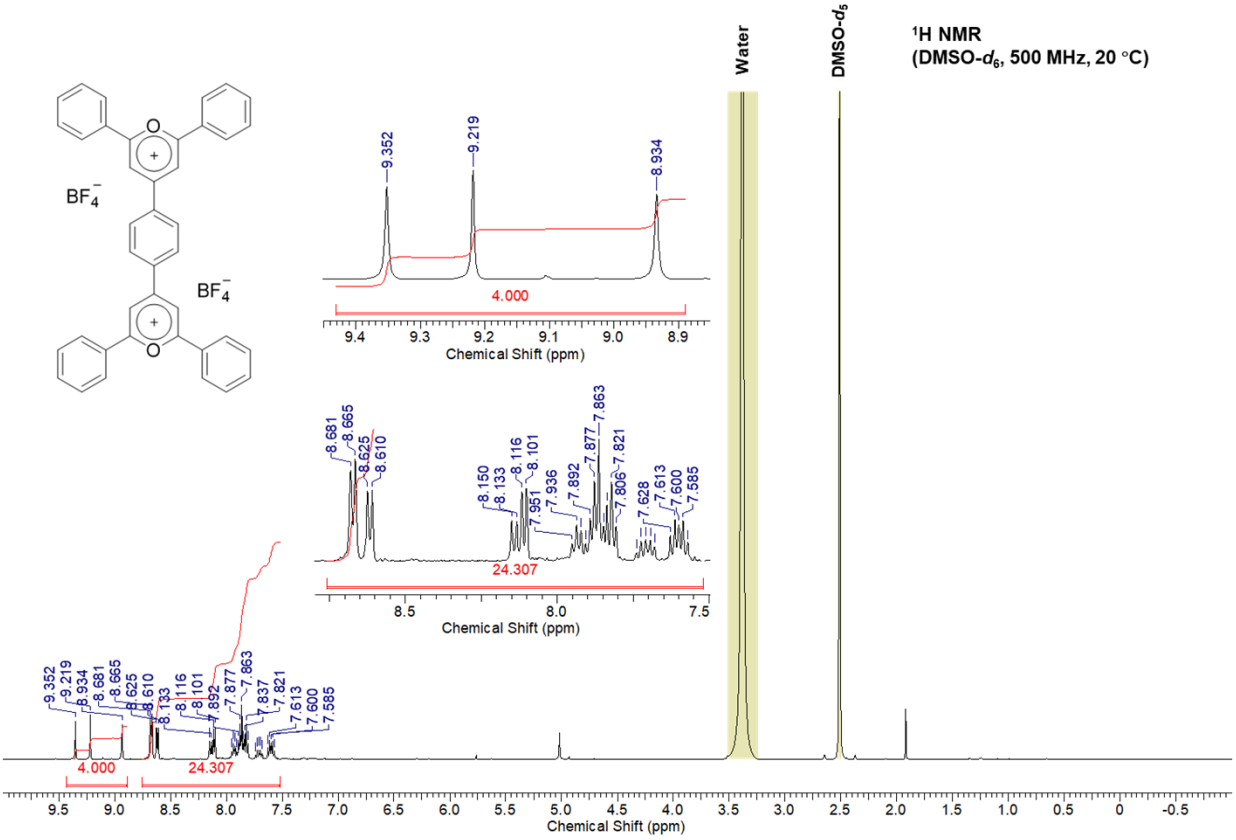

Fig. S4. ^{1}H NMR spectrum of $DP8^{2+}\cdot(BF_4^-)_2$.

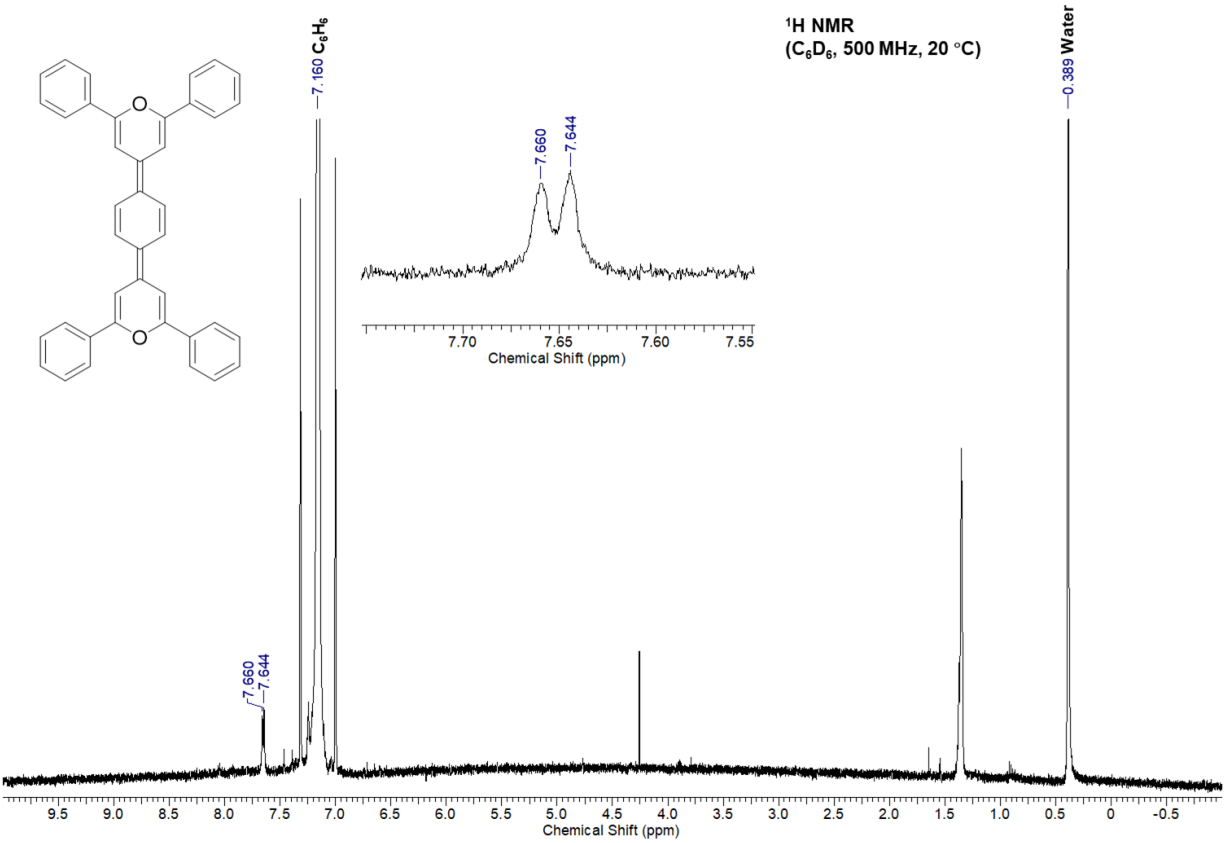

Fig. S5. ^{1}H NMR spectrum of DP8.

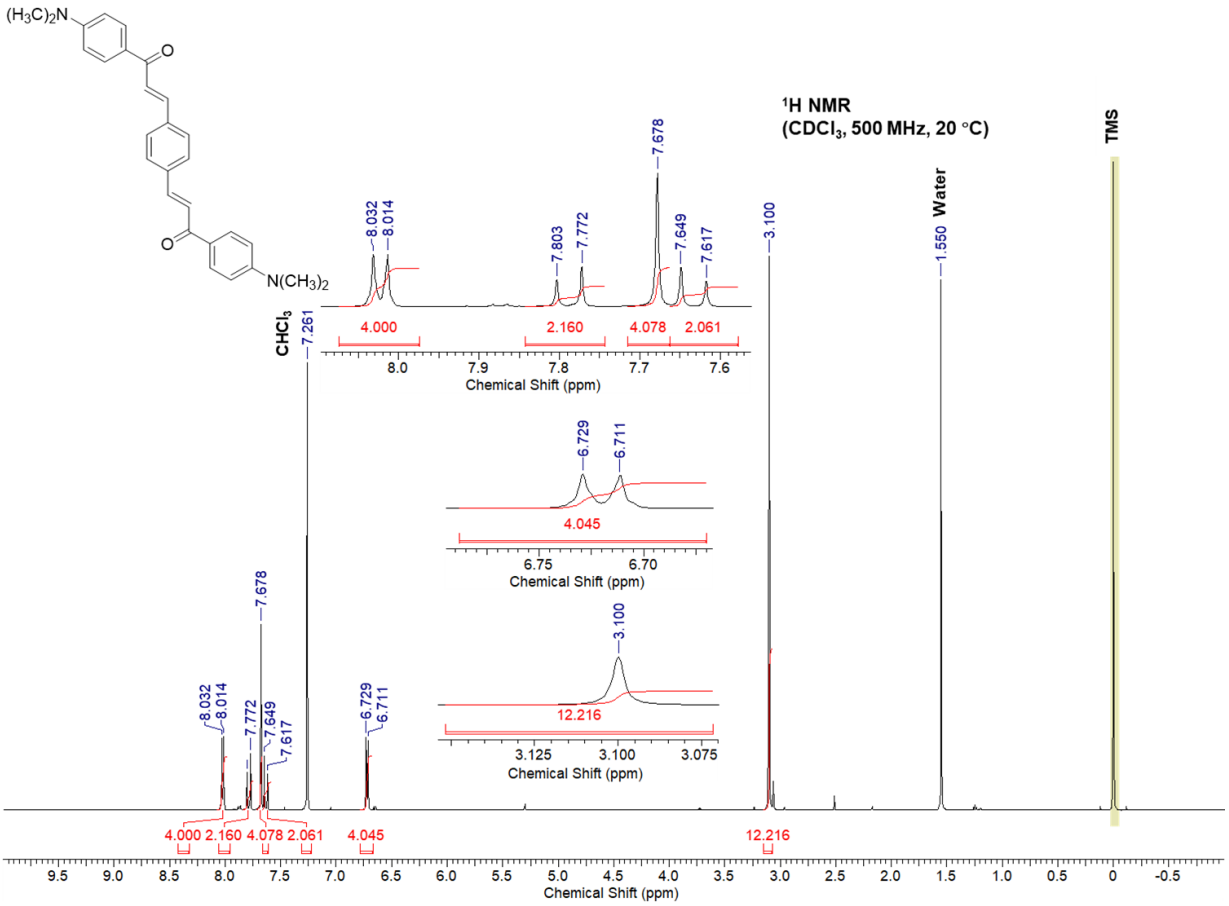

Fig. S6. ^{1}H NMR spectrum of **2**.

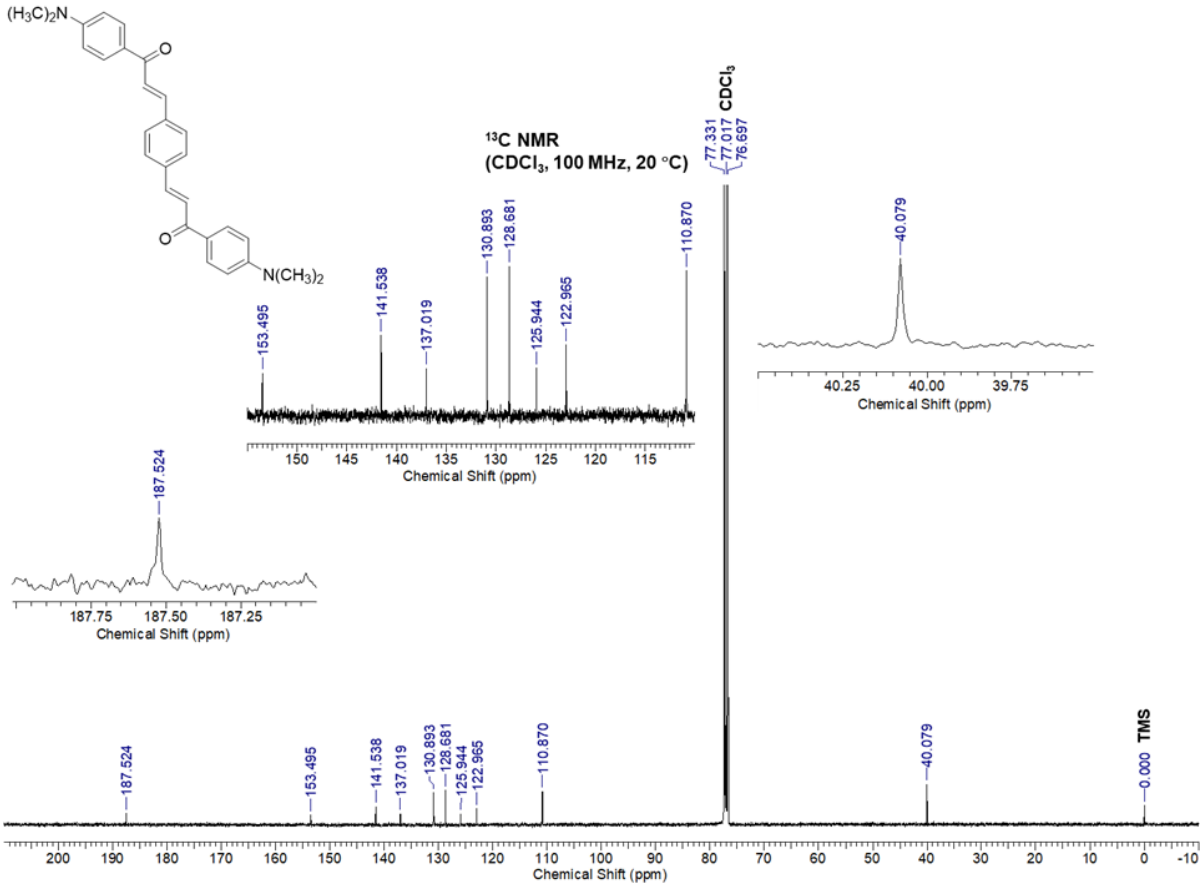

Fig. S7. ^{13}C NMR spectrum of **2**.

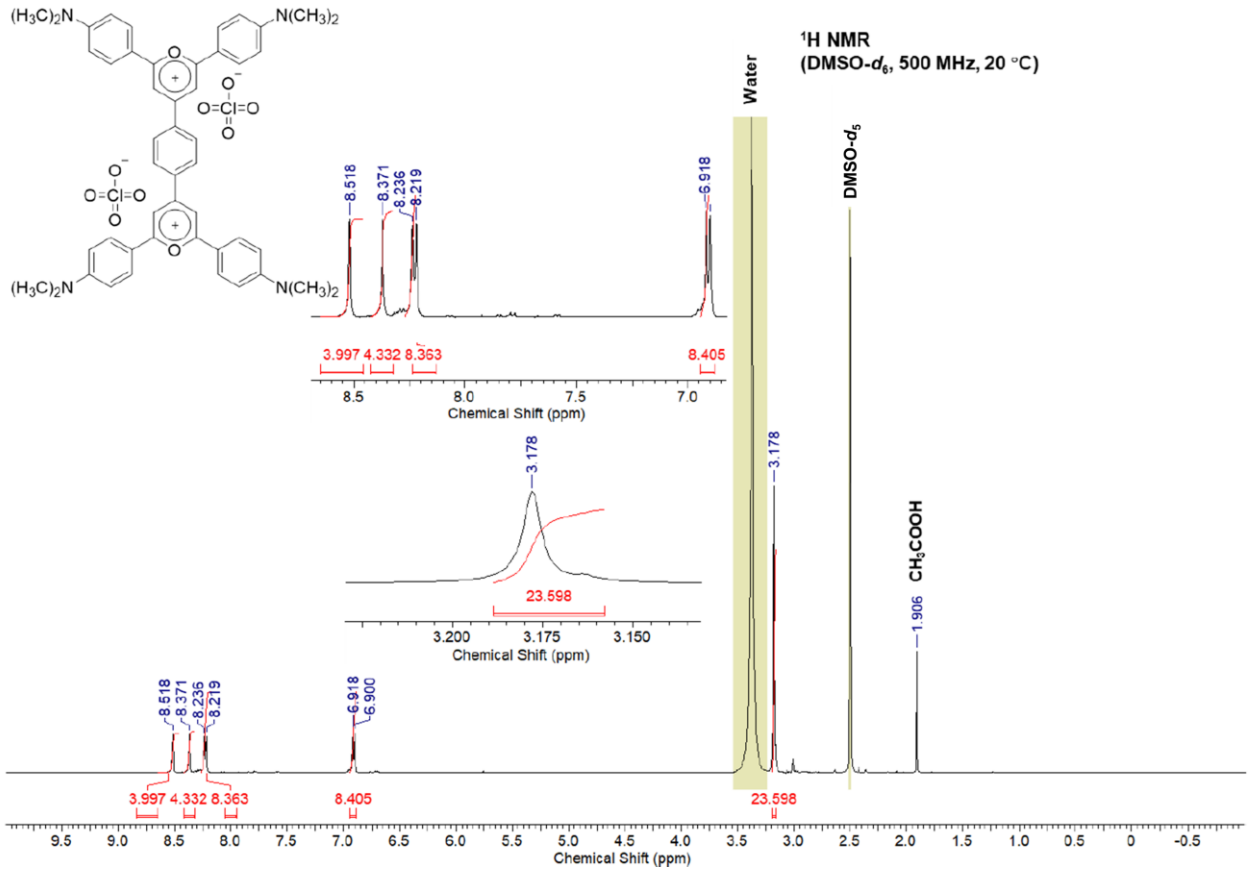

Fig. S8. ^{1}H NMR spectrum of $DP9^{2+}\cdot(ClO_4^-)_2$.

5. Differential scanning calorimetry (DSC)

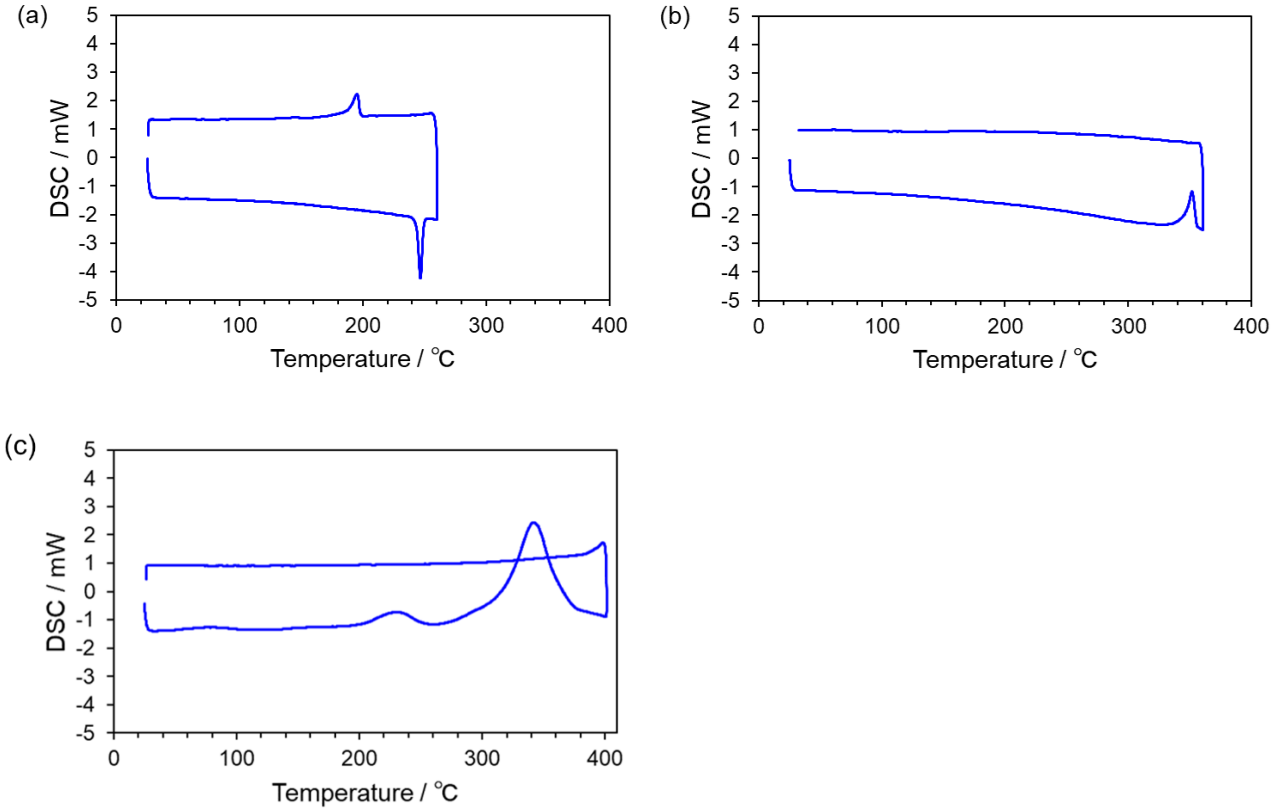

Fig. S9. Differential scanning calorimetry (DSC) curves of **2** (a), DP8 (b), and (c) $DP9^{2+}\cdot(ClO_4^-)_2$ recorded under the nitrogen flow (50 mL min^{-1}) at the heating and cooling rate of 10 °C min^{-1}. Note that DP8 and $DP9^{2+}\cdot(ClO_4^-)_2$ showed only an exothermic peak, which can be assigned to decomposition.

6. Optimized molecular structures

Table S3. Optimized Cartesian coordinates (Å) of DP8 calculated with the B3LYP / 6-311G* level (no imaginary frequencies). Total energy is −1691.8801 hartree.

Atoms	X	Y	Z
C	-5.084203	-5.980124	0.86896
C	-4.672491	-7.234618	0.575488
C	-5.018991	-8.30589	1.306756
C	-5.805361	-8.161235	2.380587
C	-6.231648	-6.933242	2.701943
C	-5.875296	-5.872221	1.959083
C	-1.377817	-4.032586	-4.787001
C	-1.038934	-5.31854	-4.943458
C	-1.508171	-6.215877	-4.067645
C	-2.300618	-5.822089	-3.058
C	-2.171767	-3.655925	-3.770956
C	-2.663134	-4.532936	-2.868028
C	-4.68192	-4.954934	0.068281
O	-3.877667	-5.243469	-0.997046
C	-3.470207	-4.228249	-1.814542
C	-3.87902	-2.97178	-1.542249
C	-4.671844	-2.633974	-0.500974
C	-5.045694	-3.672974	0.278563
C	-6.275027	2.633737	0.500266
C	-6.104345	3.632706	-0.394103
C	-6.479211	4.91251	-0.190175
O	-7.069323	5.243309	0.996164
C	-7.262599	4.270295	1.934721
C	-6.864803	3.011627	1.656262
C	-6.300352	5.89367	-1.117174
C	-7.846139	4.619005	3.11448
C	-8.206816	5.908503	3.305531
C	-8.786663	6.344063	4.435353
C	-9.0333	5.490508	5.43686
C	-8.690373	4.205356	5.282669
C	-8.110888	3.786534	4.145388
C	-6.713845	7.147792	-0.824664
C	-6.579885	8.177274	-1.675915
C	-6.016034	7.988884	-2.875501
C	-5.593933	6.760061	-3.199275
C	-5.735869	5.741182	-2.335349
C	-5.883806	1.348197	0.256003
C	-5.192234	0.958513	-0.835573
C	-4.804064	-0.306564	-1.074449
C	-5.063069	-1.348483	-0.256537
C	-5.757551	-0.959379	0.8334
C	-6.139859	0.306858	1.075599
H	-4.023013	-7.448127	-0.290363
H	-4.658083	-9.310414	1.027075
H	-6.09534	-9.034749	2.987416
H	-6.880041	-6.800029	3.585137
H	-6.282557	-4.915163	2.316713
H	-0.998233	-3.282658	-5.502348
H	-0.387592	-5.631983	-5.775837
H	-1.239415	-7.280012	-4.181182
H	-2.639668	-6.628667	-2.38603
H	-2.384153	-2.577171	-3.741674

H	-3.52567	-2.181443	-2.205241
H	-5.699318	-3.476762	1.129046
H	-5.648528	3.397525	-1.356384
H	-7.020231	2.26026	2.431056
H	-8.041892	6.680905	2.535286
H	-9.062737	7.406757	4.544735
H	-9.508962	5.838543	6.368496
H	-8.888687	3.491113	6.100411
H	-7.874034	2.712606	4.129905
H	-7.189335	7.39548	0.139531
H	-6.933404	9.183233	-1.392021
H	-5.901565	8.827856	-3.581439
H	-5.12684	6.591184	-4.18492
H	-5.353247	4.77929	-2.706926
H	-4.877863	1.664693	-1.618612
H	-4.256854	-0.421602	-2.022071
H	-6.055737	-1.662405	1.625568
H	-6.703155	0.418723	2.014147

Table S4. Optimized Cartesian coordinates (Å) of DP9 calculated with the B3LYP / 6-311G* level (no imaginary frequencies). Total energy is −2227.8669 hartree.

Atoms	X	Y	Z
C	-4.512491	-5.998614	0.748027
C	-4.112486	-7.255013	0.464994
C	-4.539333	-8.331712	1.145101
C	-5.407048	-8.255289	2.174461
C	-5.803266	-6.99733	2.456656
C	-5.377703	-5.918219	1.777764
C	-0.357158	-3.999884	-4.562568
C	0.017161	-5.279528	-4.766203
C	-0.561705	-6.154448	-3.918988
C	-1.427988	-5.783829	-2.96178
C	-1.223823	-3.626299	-3.605571
C	-1.798393	-4.503069	-2.75908
C	-4.034358	-4.962341	0.007086
O	-3.158745	-5.239963	-1.00344
C	-2.67961	-4.21193	-1.764
C	-3.09055	-2.955747	-1.494377
C	-3.950918	-2.631121	-0.503983
C	-4.394113	-3.680396	0.223392
C	-5.54869	2.630993	0.503489
C	-5.398434	3.624987	-0.399792
C	-5.775384	4.903696	-0.193804
O	-6.34087	5.239819	1.00289
C	-6.509901	4.27033	1.949648
C	-6.116173	3.010854	1.669746
C	-5.624927	5.878102	-1.131525
C	-7.063372	4.623272	3.141504
C	-7.42393	5.905884	3.350173
C	-7.972708	6.336392	4.498007
C	-8.214462	5.525076	5.547603
C	-7.855189	4.242596	5.334921
C	-7.305819	3.809159	4.187391
C	-6.034756	7.132648	-0.854462
C	-5.925441	8.14943	-1.725223
C	-5.394821	8.009381	-2.956961
C	-4.983549	6.754262	-3.230073

C	-5.091834	5.735008	-2.360649
C	-5.15854	1.346088	0.257491
C	-4.442303	0.964699	-0.820918
C	-4.053512	-0.299921	-1.060456
C	-4.341073	-1.346192	-0.257976
C	-5.061869	-0.965679	0.817675
C	-5.441571	0.300677	1.062698
N	-5.290985	8.978909	-3.789737
C	-4.693284	8.738327	-5.129396
C	-5.771091	10.332583	-3.406349
N	0.845324	-5.631714	-5.679647
C	1.203291	-7.066194	-5.834629
C	1.439078	-4.60188	-6.572256
N	-5.816361	-9.28243	2.823843
C	-6.775252	-9.10993	3.94665
C	-5.328224	-10.634603	2.445278
N	-8.73714	5.934918	6.64446
C	-8.969761	4.973239	7.753925
C	-9.103154	7.367905	6.794561
H	-3.403168	-7.458844	-0.355937
H	-4.128176	-9.294332	0.800539
H	-6.510803	-6.784137	3.274482
H	-5.792077	-4.961147	2.129108
H	0.035858	-3.177314	-5.182116
H	-0.352394	-7.235398	-3.965639
H	-1.82725	-6.601171	-2.33637
H	-1.428188	-2.545615	-3.566802
H	-2.675279	-2.154469	-2.107434
H	-5.10948	-3.493357	1.025641
H	-4.967255	3.384388	-1.372672
H	-6.247257	2.263178	2.453387
H	-7.279788	6.675097	2.57163
H	-8.214651	7.41115	4.525169
H	-7.995569	3.4677	6.106115
H	-7.068511	2.734686	4.168288
H	-6.488964	7.384615	0.119601
H	-6.30397	9.118208	-1.361094
H	-4.528634	6.493346	-4.199557
H	-4.710341	4.771692	-2.731635
H	-4.10227	1.679254	-1.585716
H	-3.485686	-0.413183	-1.996331
H	-5.379619	-1.676052	1.595835
H	-6.031642	0.409789	1.985238
H	-5.296655	8.011894	-5.720079
H	-4.676874	9.674713	-5.729638
H	-3.631179	8.412625	-5.048897
H	-5.202319	10.735692	-2.537648
H	-5.61155	11.058371	-4.234099
H	-6.867464	10.335359	-3.209736
H	1.708272	-7.460746	-4.923602
H	0.314444	-7.681061	-6.103936
H	1.929322	-7.205566	-6.665784
H	0.658069	-4.089785	-7.179264
H	2.051468	-3.869599	-5.998285
H	2.13434	-5.066857	-7.305609
H	-7.74068	-8.679621	3.595286
H	-7.031291	-10.091511	4.403061
H	-6.334818	-8.500566	4.768435
H	-4.226075	-10.722297	2.580171

H	-5.775048	-11.414657	3.100421
H	-5.632321	-10.901709	1.407573
H	-8.013309	4.536873	8.12194
H	-9.425411	5.483419	8.631106
H	-9.691434	4.177827	7.45877
H	-9.88532	7.66767	6.060408
H	-9.541817	7.5614	7.798298
H	-8.207578	8.026485	6.724603

7. Diradical characters estimated by theoretical calculations

The diradical character (y) of DP8 and DP9 and their non-extended counterparts (DP0 and DP7) were calculated with the Gaussian 16 program [1] using the RB3LYP/6-311G* level of theory for the structural optimization and the LC-UB3LYP/6-31+G* level of theory for the occupancy of the highest occupied natural orbital (n_{HONO}) and the lowest unoccupied natural orbital (n_{LUNO}) by following equation; [3]

$$y = 1 - \frac{2T}{1+T^2} \quad \text{where } T = \frac{n_{HONO} - n_{LUNO}}{2}$$

As summarized in Fig. S10, the y values of DP8 and DP9, 0.21 and 0.20, respectively, indicated that the open-shell diradical character could not be ignored in DP8 and DP9, which are contrasted to their non-extended counterparts.

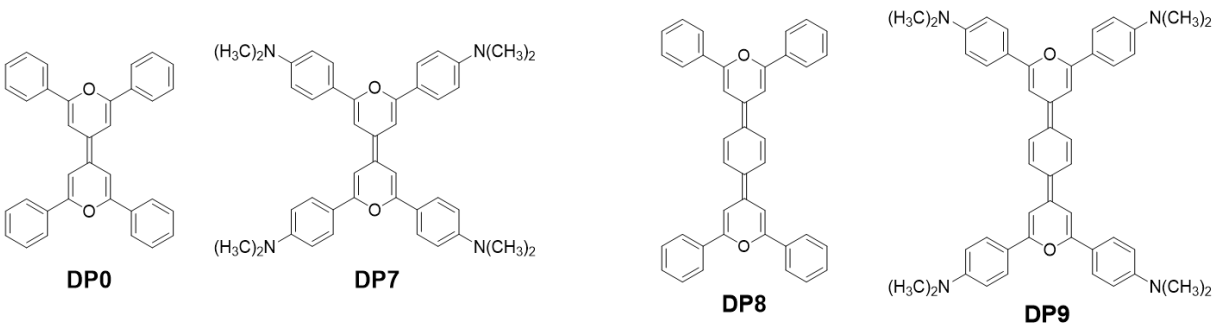

Fig. S10. Calculated diradical character (y) of DP8 and DP9 together with their non-extended counterparts.

8. References

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