Electronic Supplementary Information (ESI)

The "flexible" carborane-based luminogen: variable emission behaviours in aggregates

Jiaxin Li,[a] Jingkai Xu, [a] Linbo Yan,[b] Changsheng Lu*[a] and Hong Yan*[a]

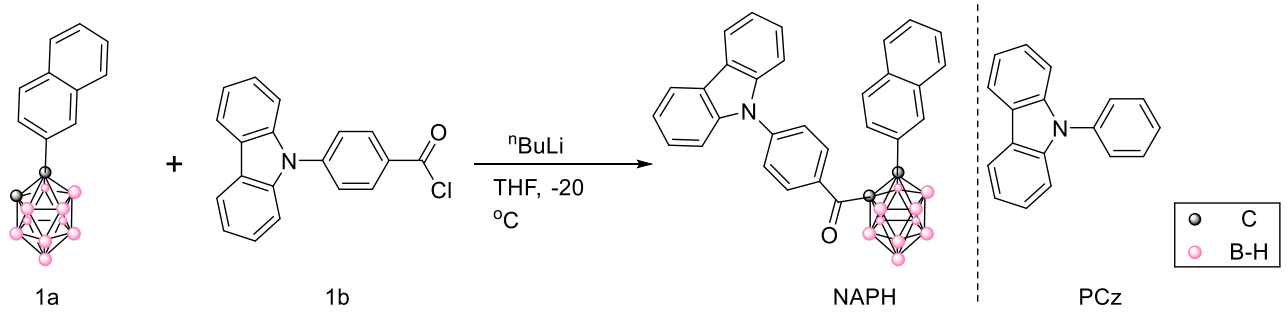
[a]*State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China*
[b]*Sports Biochemistry Lab, College of Physical Education and Health, Guangxi Normal University, Guilin 541006, China*

CONTENS

I General Methods

All air- and moisture-sensitive reactions were carried out under an argon atmosphere. THF was dried over sodium and distilled under nitrogen. Compound **PCz** was commercially available. ^{1}H, ^{13}C and ^{11}B NMR spectra were measured at room temperature by using Bruker 400. $CDCl_3$ was used as deuterated reagent unless specified. Mass spectra were measured by ESI-MS (LCQ Fleet, Thermo Fisher Scientific). Photoluminescence spectral measurements were carried out by using a Hitachi F-4600 photoluminescence spectrophotometer. Electronic absorption spectra were recorded with Shimadzu UV-2550 spectrophotometers. Thermogravimetric analysis (TGA) of samples were conducted by Mettler TGA2. The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer using the ω-2θ scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2014. All calculations and molecular graphics were carried out on a computer using Mercury 3.10.3. The powder XRD patterns were recorded at room temperature on a BRUKER D8 ADVANCE X-ray diffractometer.

II Synthesis



Scheme S1 Synthetic route for **NAPH**.

To a solution of naphthalenyl carborane (**1a**, 270.2 mg, 1.0 mmol) in dry THF (20.0 mL) was added dropwise *n*-BuLi (1.6 M in n-hexane, 1.1 mmol, 0.69 mL) at -20 ℃. After stirring for 2h, 4-(9H-Carbazol-9-yl)benzoyl chloride (**1b**, 242.2 mg, 1.1 mmol) in THF (5.0 mL) was added dropwise *via* a syringe. The resulting mixture was stirred at -20 ℃ for additional 2h. After that, the mixture was quenched by addition of saturated aqueous NH_4Cl solution (10 mL), and extracted with DCM (20 mL∗3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated by reduced pressure. The crude product was purified by silica gel column chromatography using DCM/n-hexane (6:1, V:V) as the eluent to give **NAPH** as a white powder (285.8 mg, 53%).m. p. 185.0-186.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 8.10 (s, 1H),7.84-7.78 (m, 3H), 7.72-7.65 (m, 3H), 7.58-7.49 (m, 4H), 7.44-7.37 (m, 4H), 7.32 (t, J = 7.2 Hz, 2H), 3.32-1.91(10H, B-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 142.0, 139.9, 134.2, 133.7, 132.3, 131.5, 130.7, 128.8, 128.3, 128.1, 128.0, 127.5, 127.3, 127.2, 126.3, 125.6, 123.9, 120.8, 120.5, 109.6, 85.6, 82.9. ^{11}B NMR (160 MHz, $CDCl_3$) δ -0.4 (1B), -2.9 (1B), -9.5(8B). $C_{31}H_{29}B_{10}NO$ calcd: C, 68.99; H, 5.42; N, 2.60. Found: C, 68.87; H, 5.43, N, 2.60.

III Supplementary Figures

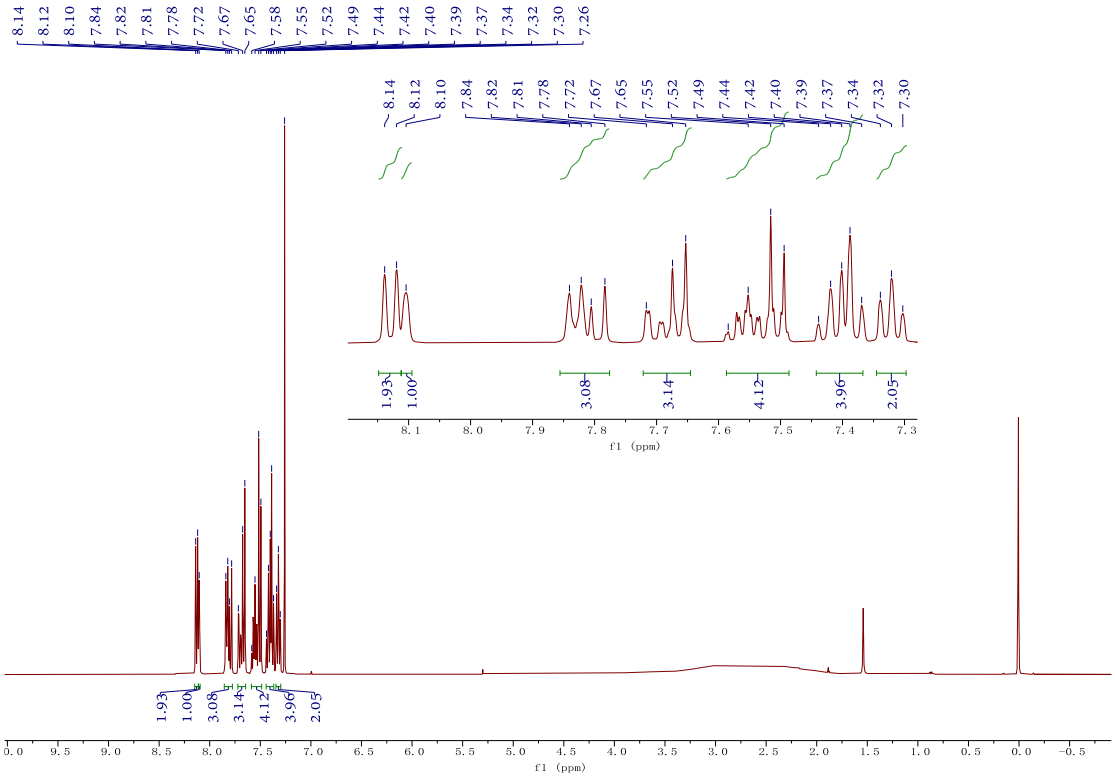


Fig. S1 ^{1}H NMR spectrum of **NAPH** measured in $CDCl_3$.

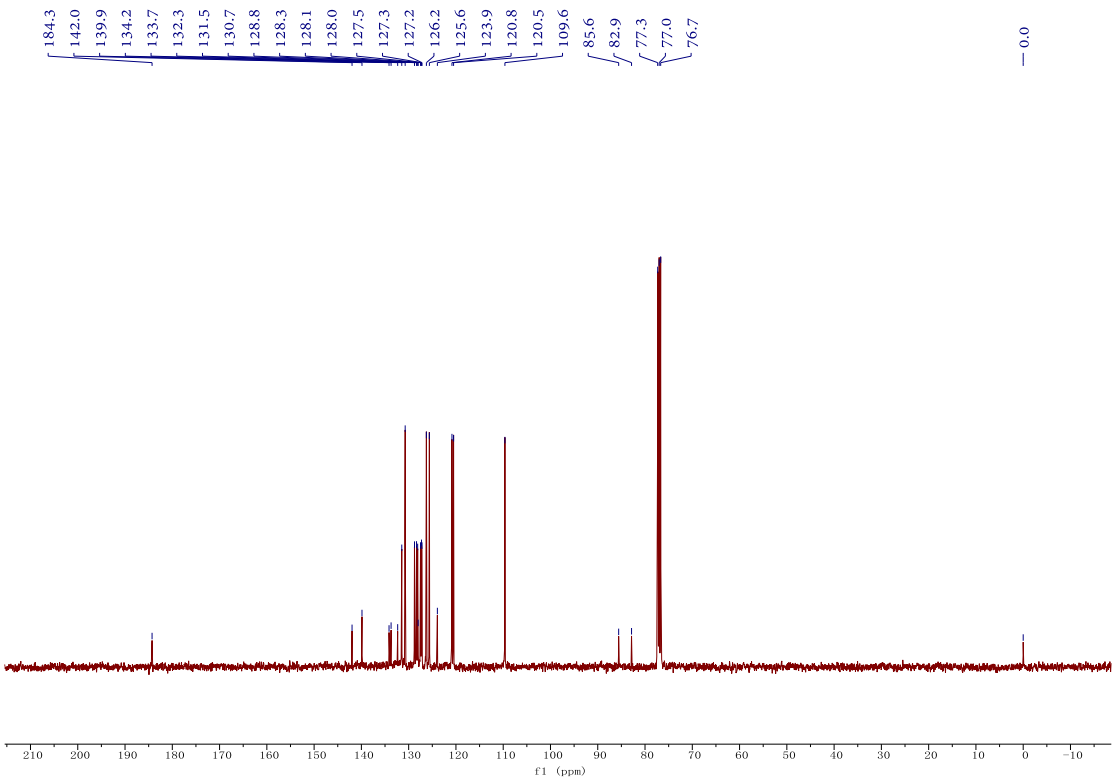


Fig. S2 ^{13}C NMR spectrum of **NAPH** measured in $CDCl_3$.

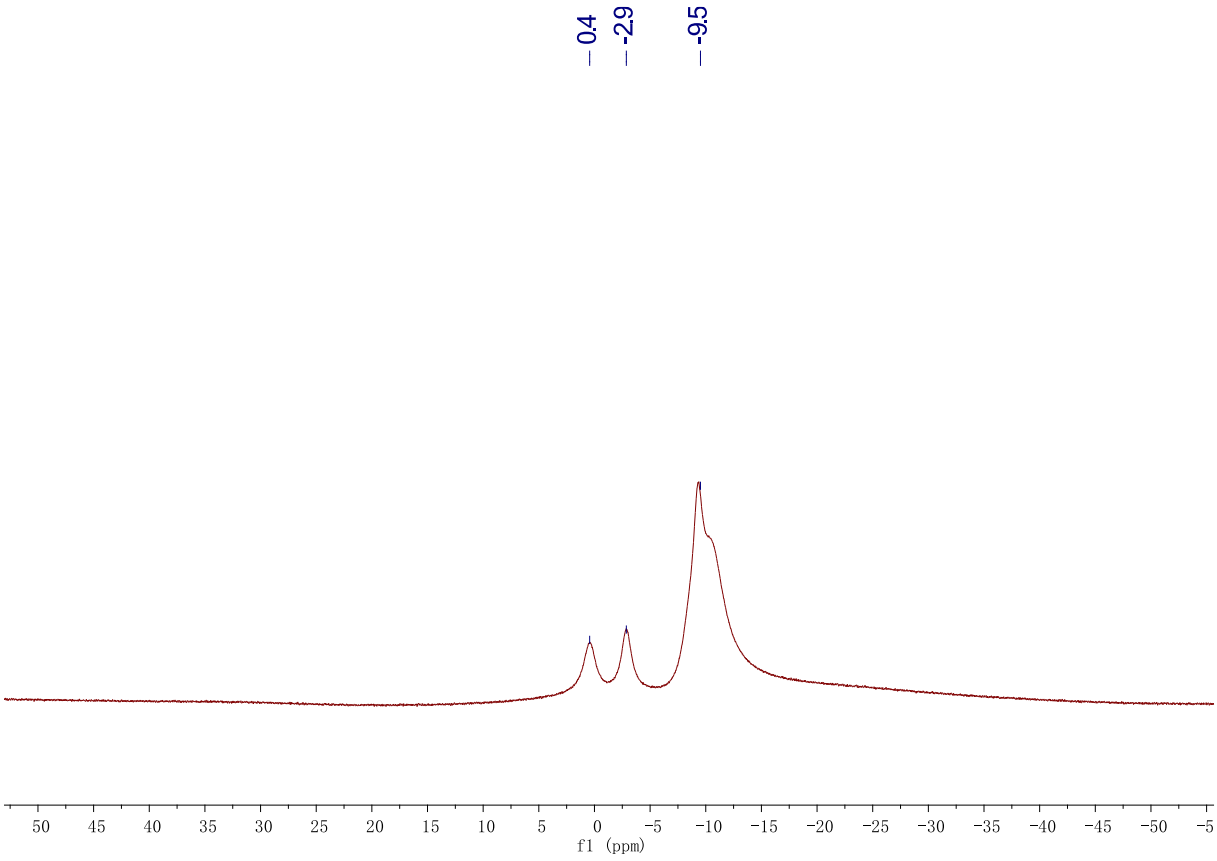


Fig. S3 ^{11}B NMR spectrum of **NAPH** measured in $CDCl_3$.

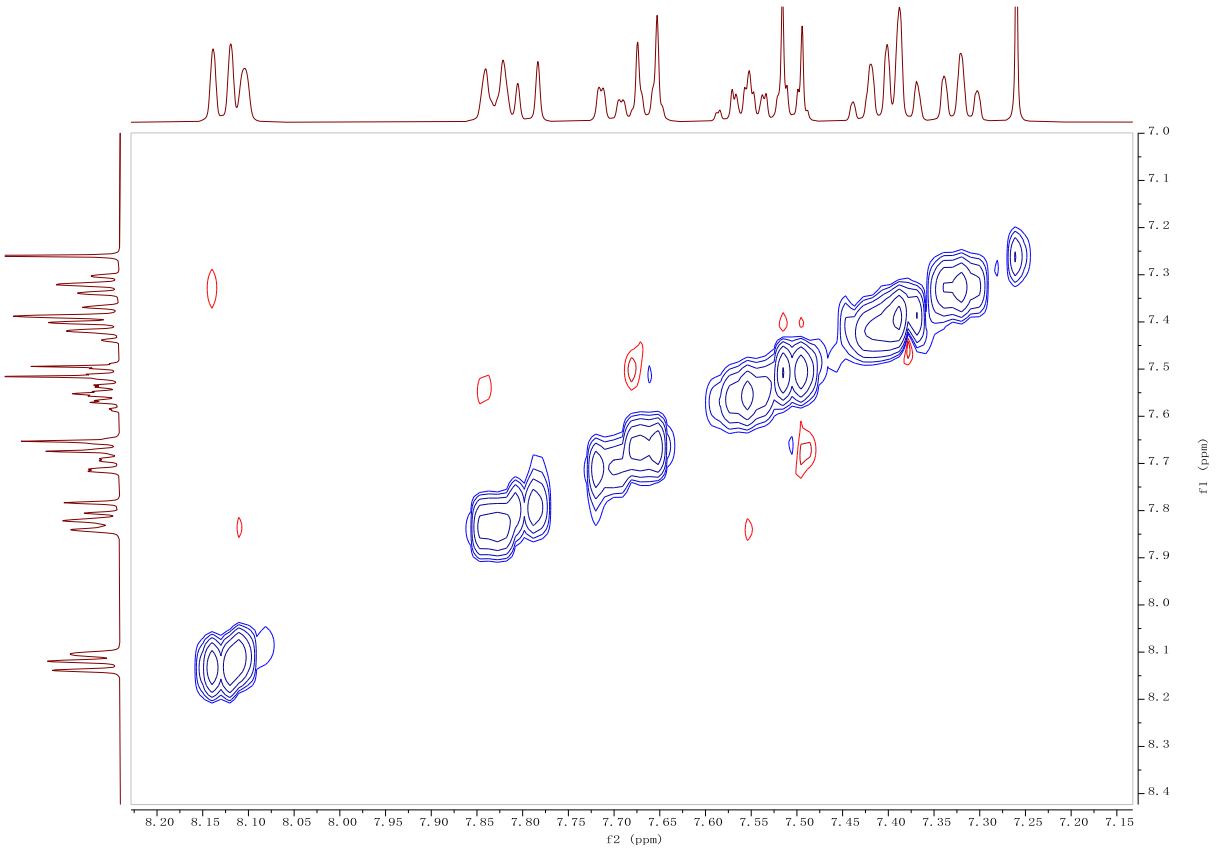


Fig. S4 NOESY ^{1}H-^{1}H spectrum of **NAPH** measured in $CDCl_3$.

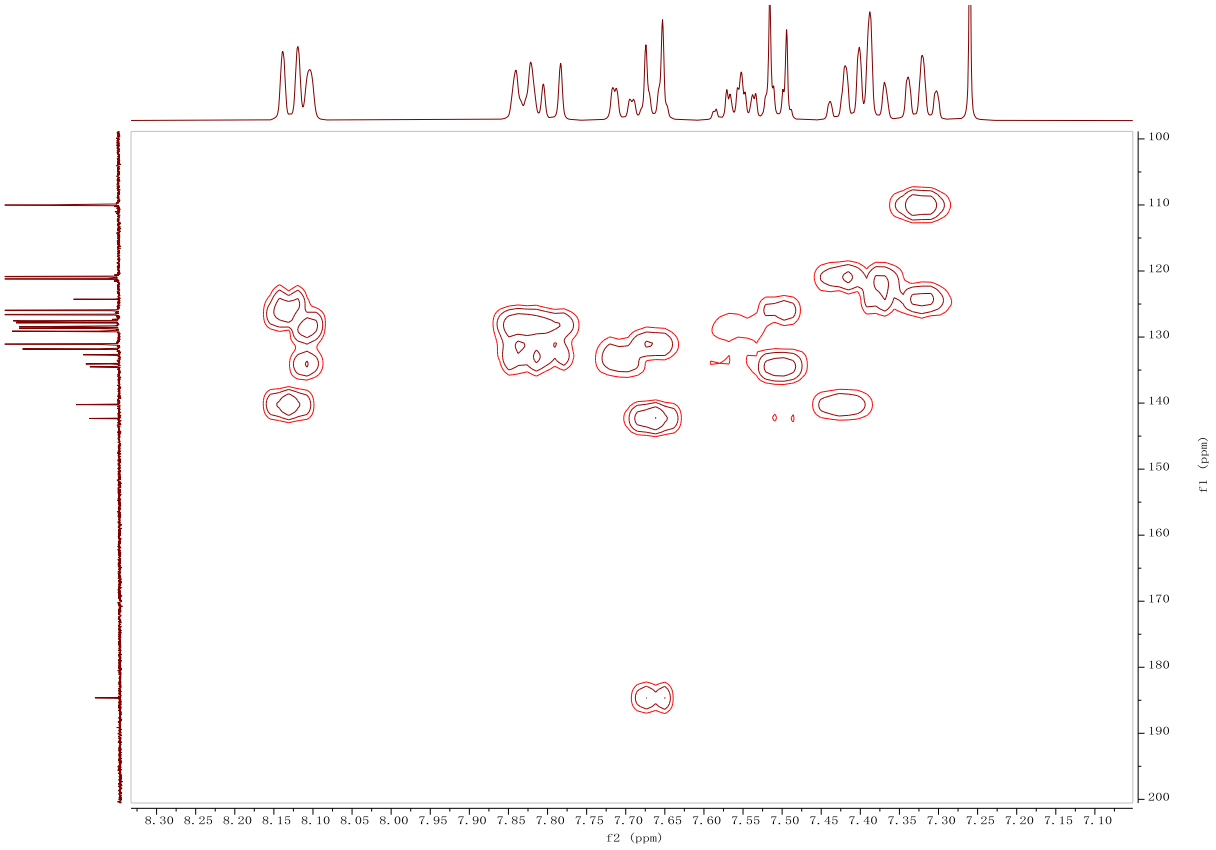


Fig. S5 HMBC ^{1}H-^{13}C spectrum of **NAPH** measured in $CDCl_3$.

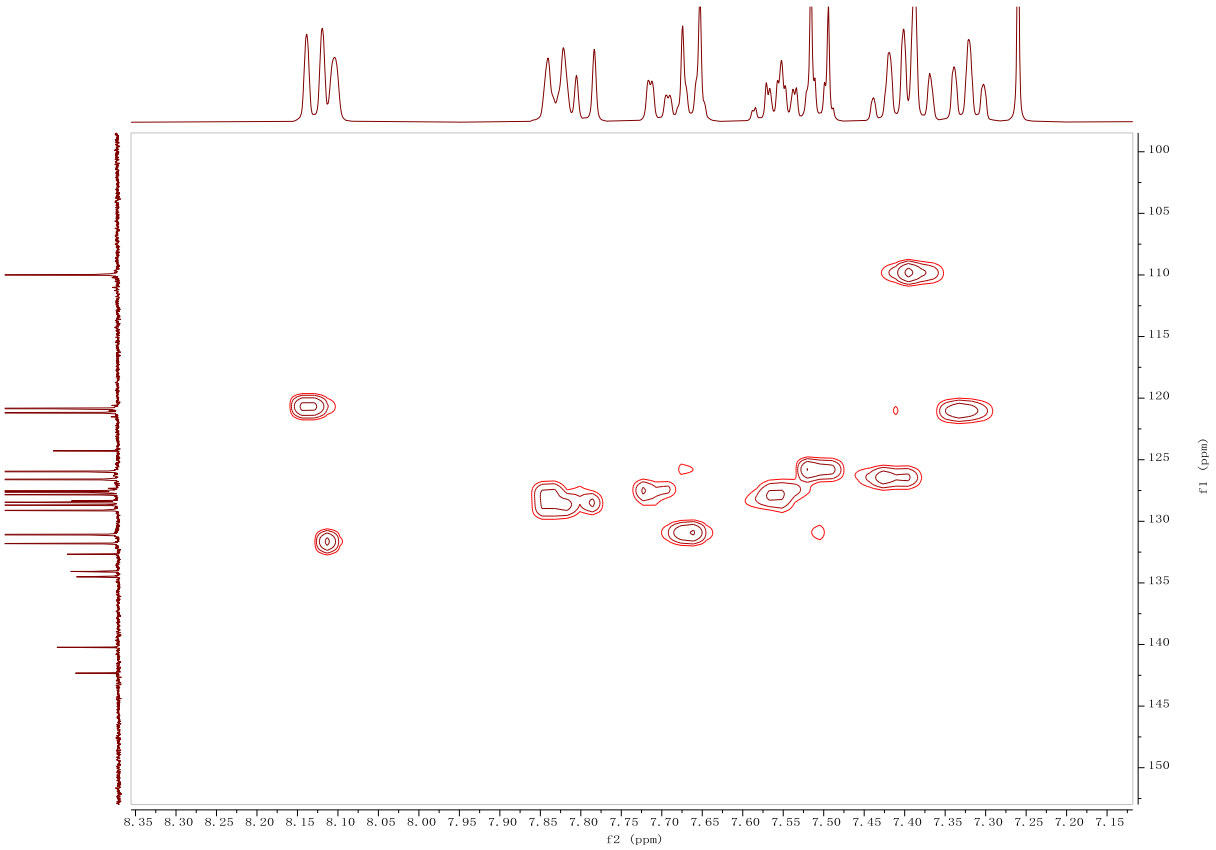


Fig. S6 HSQC ^{1}H-^{13}C spectrum of **NAPH** measured in $CDCl_3$.

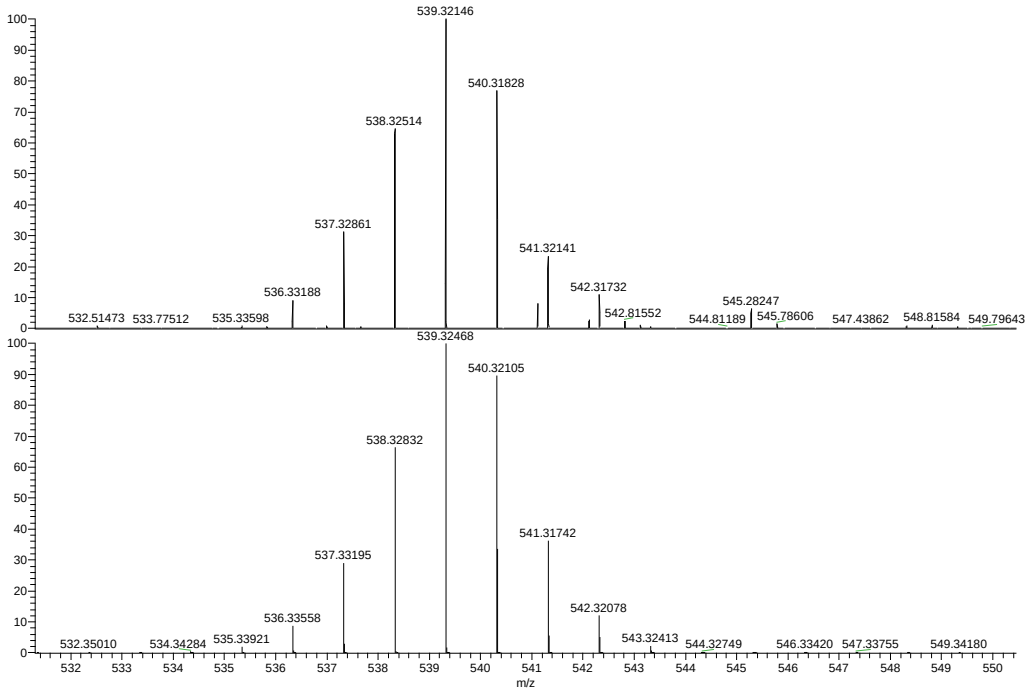


Fig. S7 HRMS of **NAPH** (up) and calculated (down).

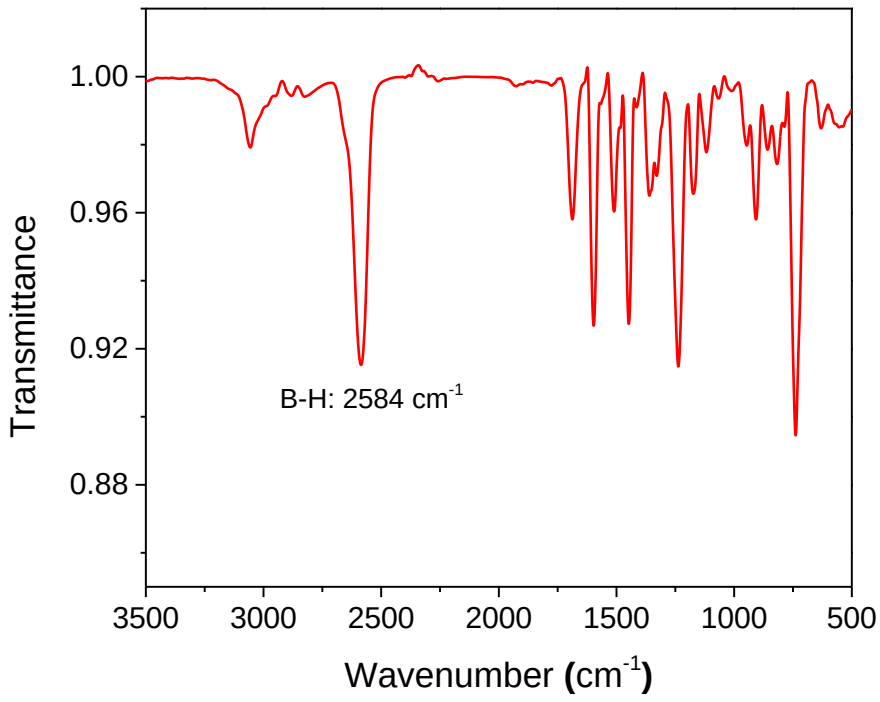
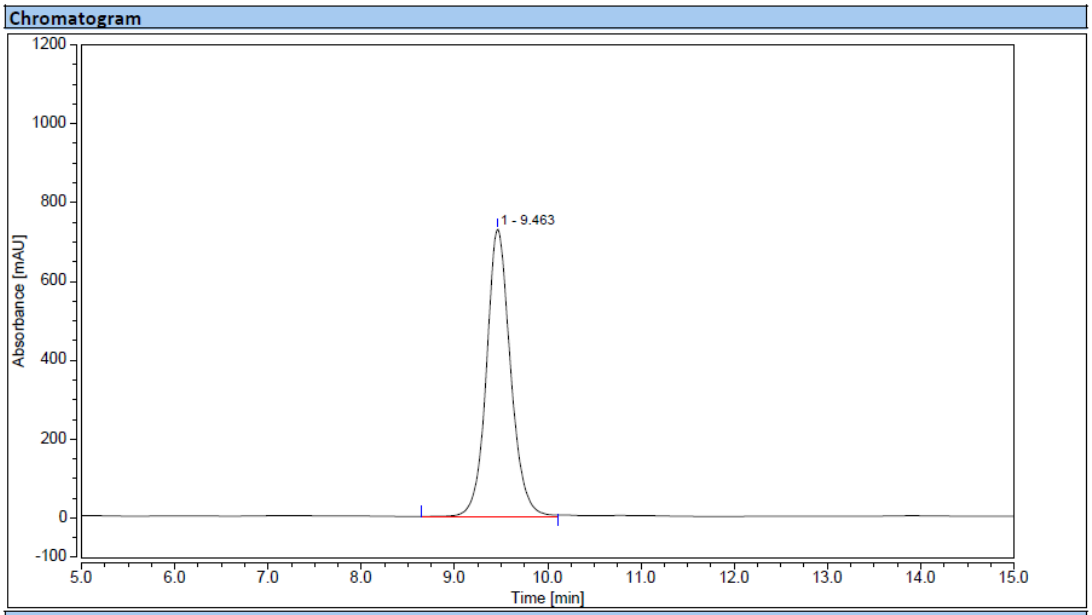


Fig. S8 FT-IR spectrum for **NAPH**. IR (KBr): (ν cm^{-1}) 2584 (B−H).



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.463	217.423	729.203	100.00	100.00	n.a.
Total:			**217.423**	**729.203**	**100.00**	**100.00**	

Fig. S9 HPLC profile of **NAPH** with *n*-hexane and isopropanol as eluent with the ratio of 90:10 (*v*/*v*).

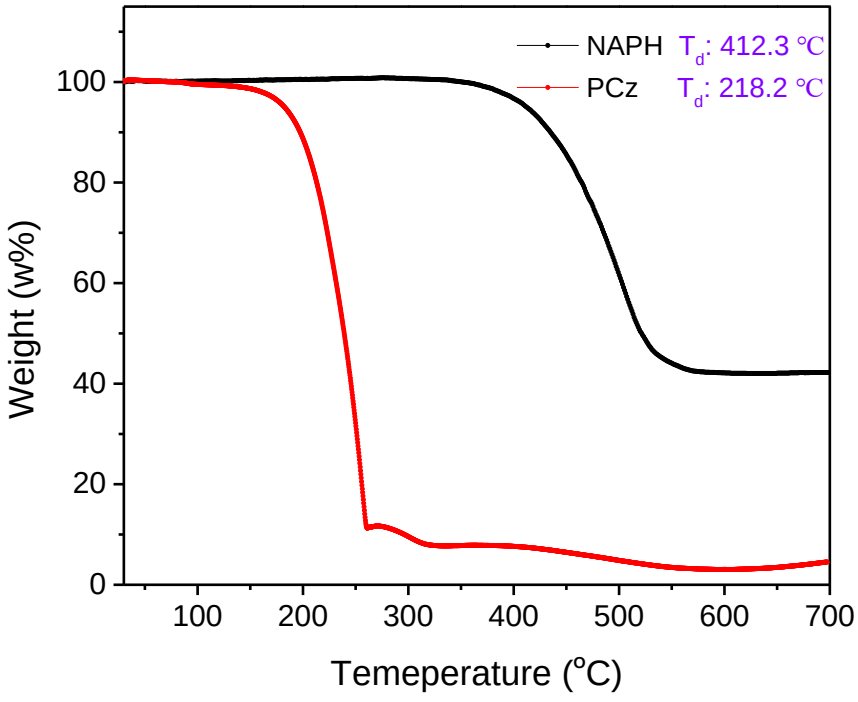


Fig. S10 TGA curves of **NAPH** and **PCz** under nitrogen. T_d is the temperature when the weight loss was 5%.

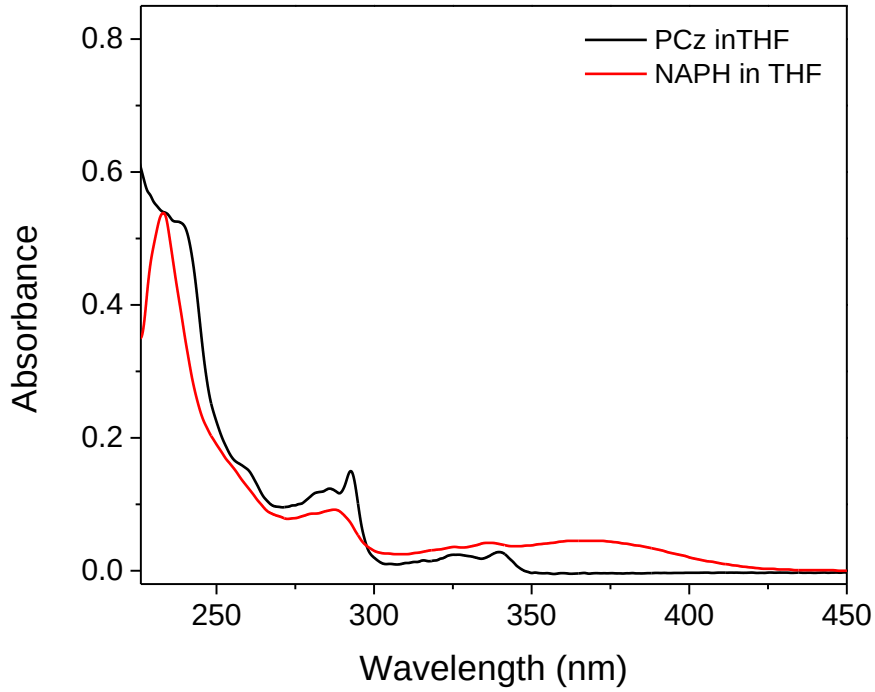


Fig. S11 UV-Vis absorption spectra of **NAPH** and **PCz** in THF ($c = 10^{-5}$ M, 25 °C).

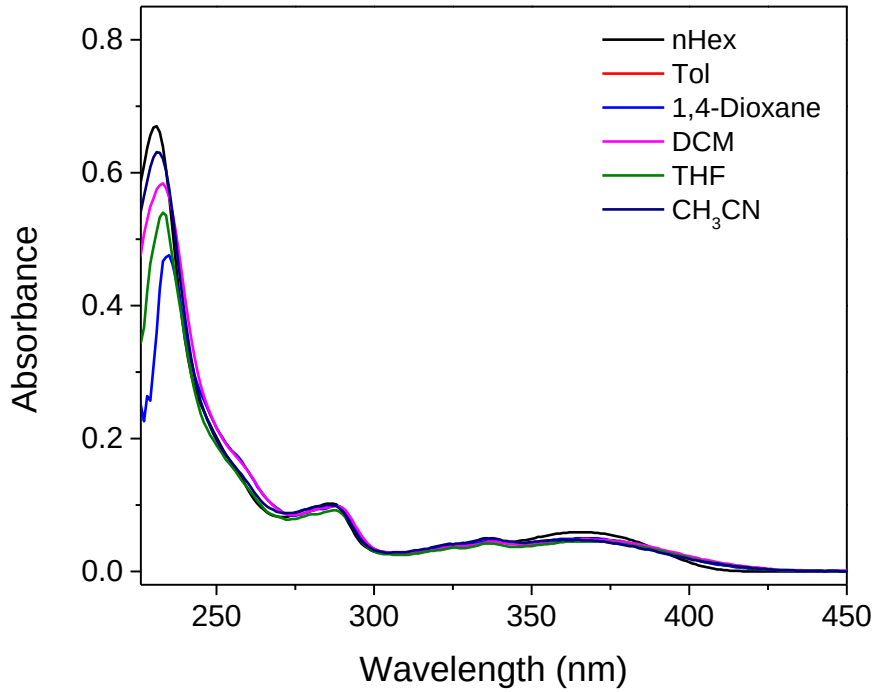


Fig. S12 UV-Vis absorption spectra of **NAPH** in various solvents ($c = 10^{-5}$ M, 25 °C).

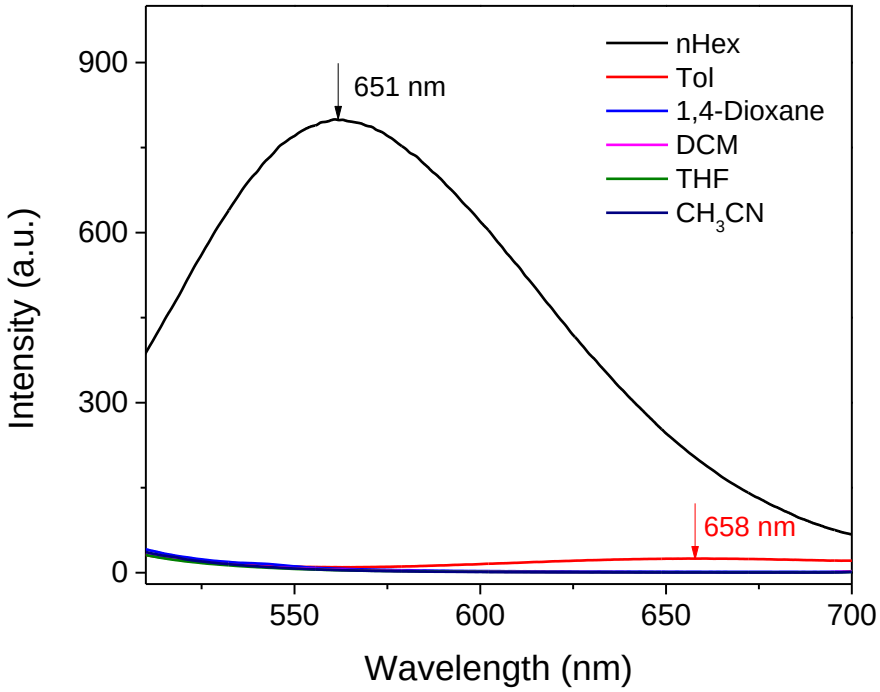


Fig. S13 PL spectra of **NAPH** in various solvents under excitation at 400 nm (c = 10^{-5} M, 25 °C).

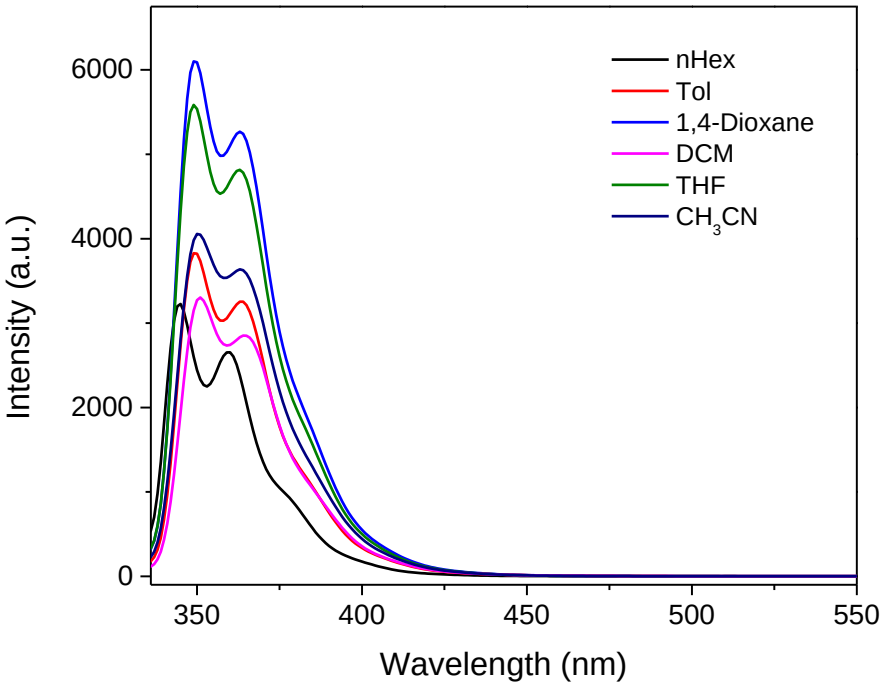


Fig. S14 PL spectra of **PCz** in various solvents under excitation at 325 nm (c = 10^{-5} M, 25 °C).

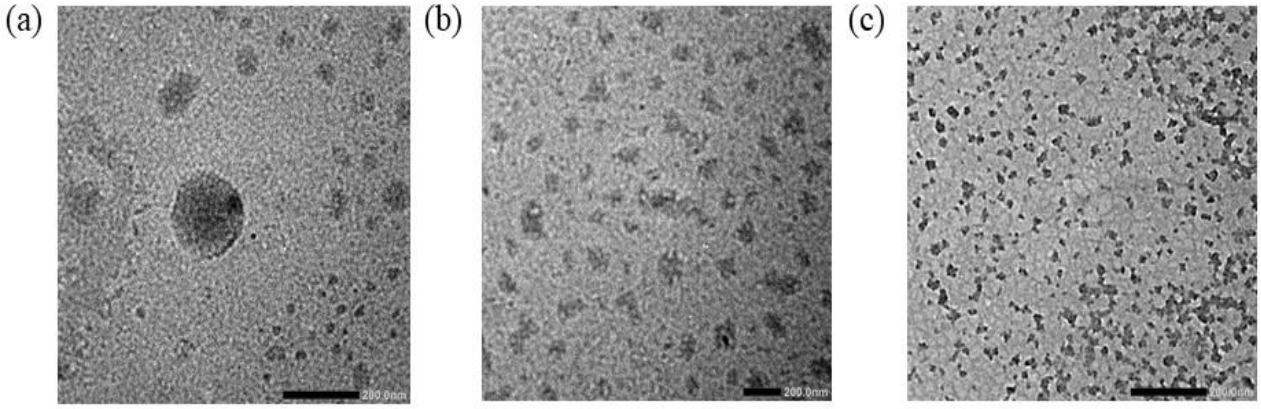


Fig. S15 Transmission electron microscopic images of **NAPH** aggregates under different water fractions. (a) 90% (b) 95% (c) 99%.

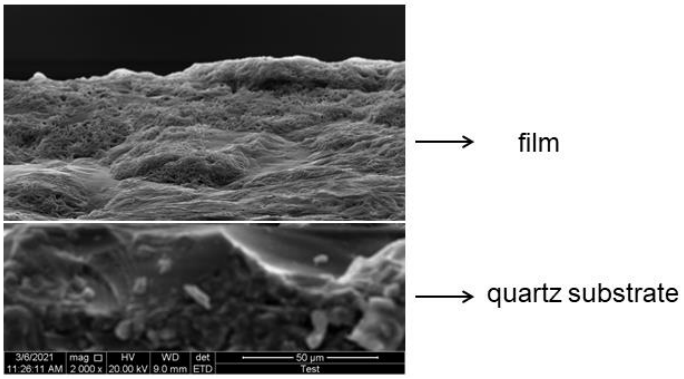


Fig.S16 Scanning electron microscopic image of **NAPH** in spin-coated film.

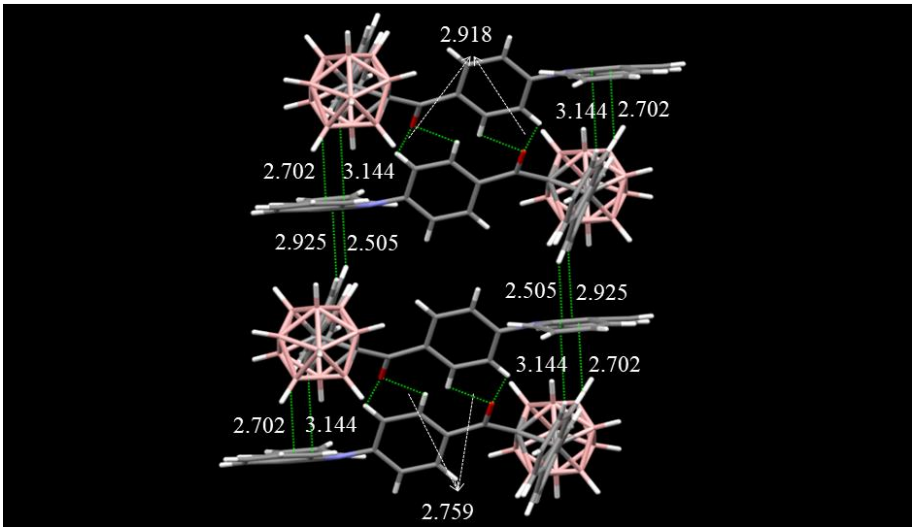


Fig. S17 Molecular stacking modes and the interactions in **O-Crystal**.

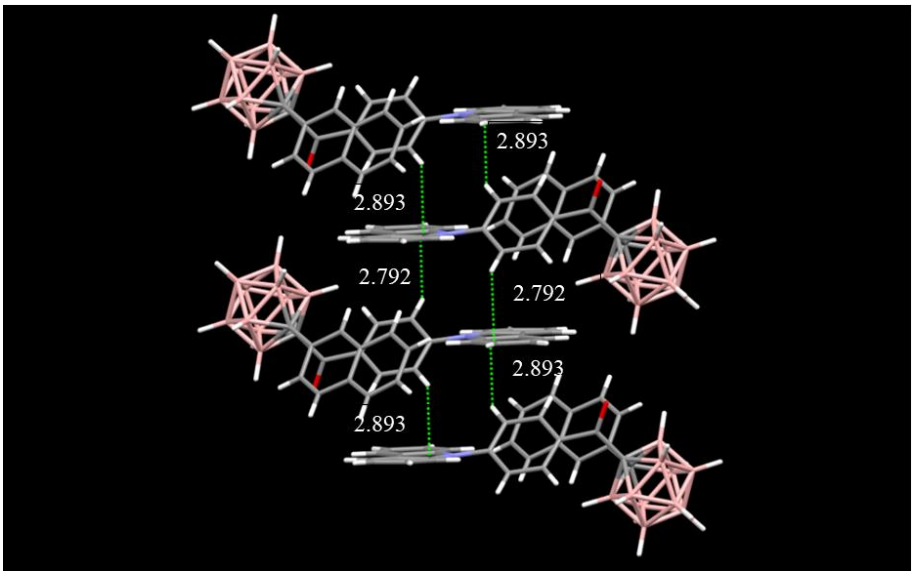


Fig. S18 Molecular stacking modes and the interactions in **R-Crystal**.

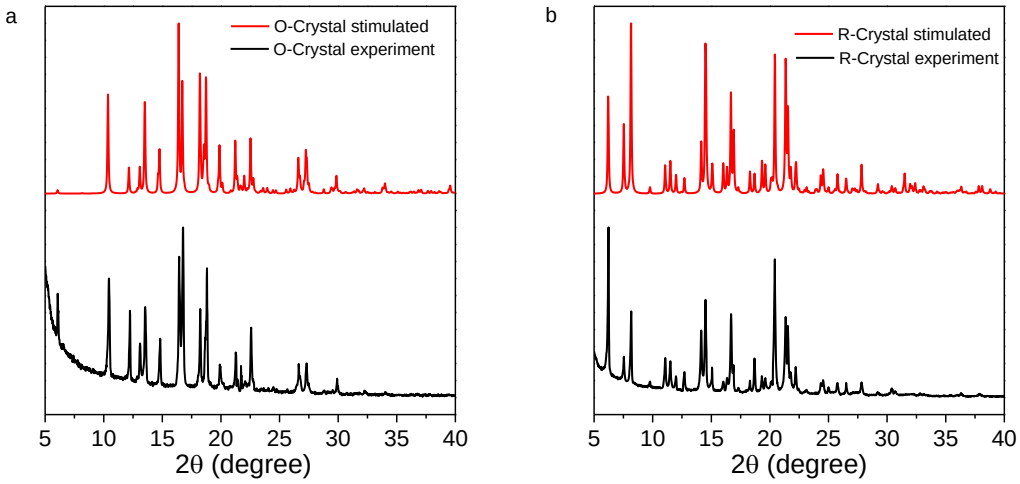


Fig. S19 Calculated and experimental PXRD patterns for (a) **O-Crystal** (b) **R-Crystal**.

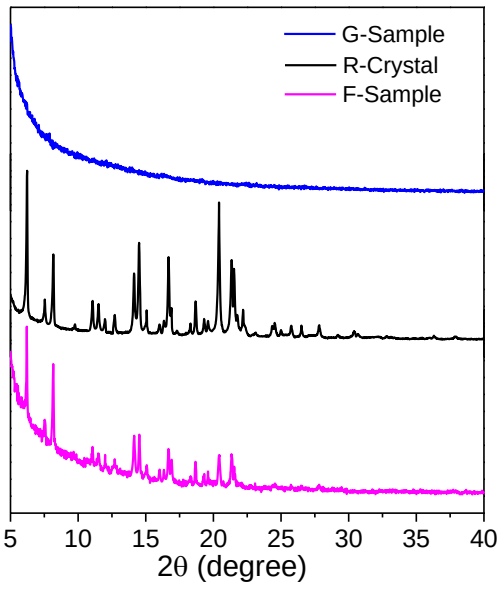


Fig. S20 PXRD patterns of **G-Sample**, **R-Crystal** and **F-Sample.**

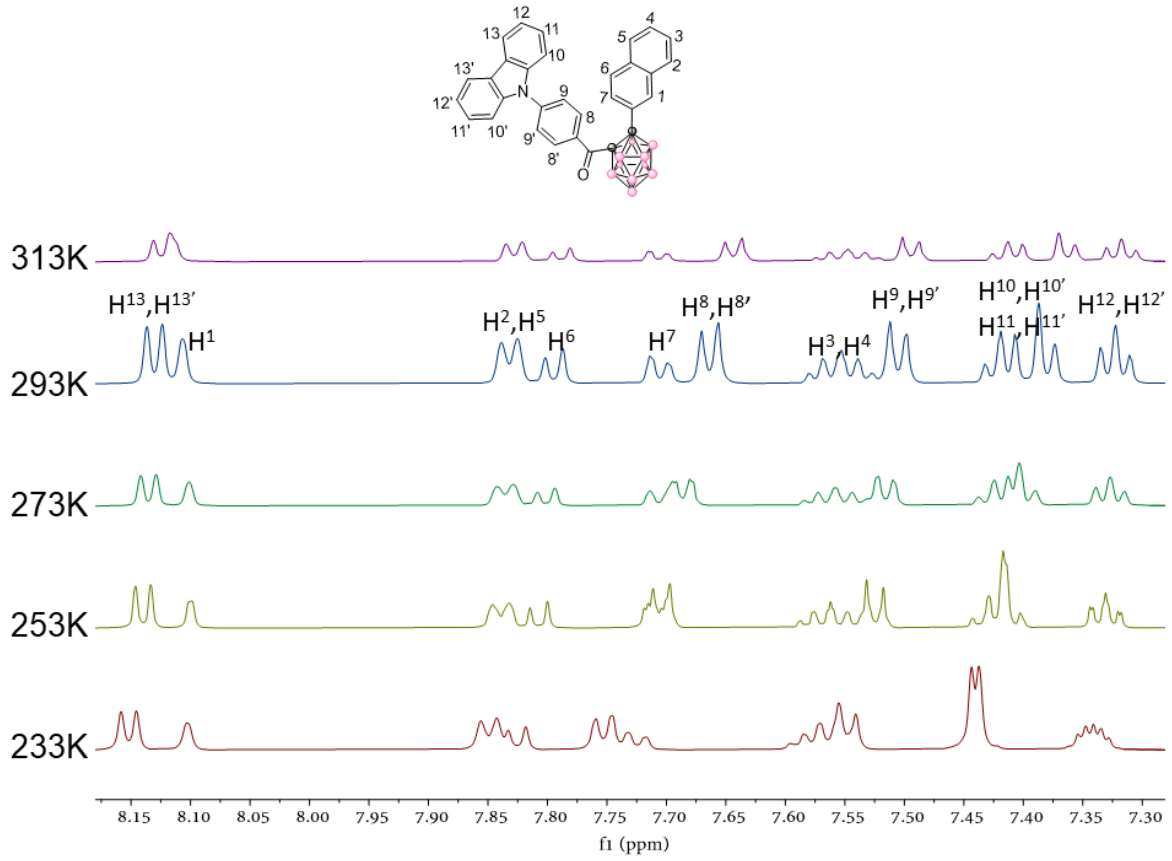


Fig. S21 ^{1}H NMR of **NAPH** from 313–233 K in $CDCl_3$.

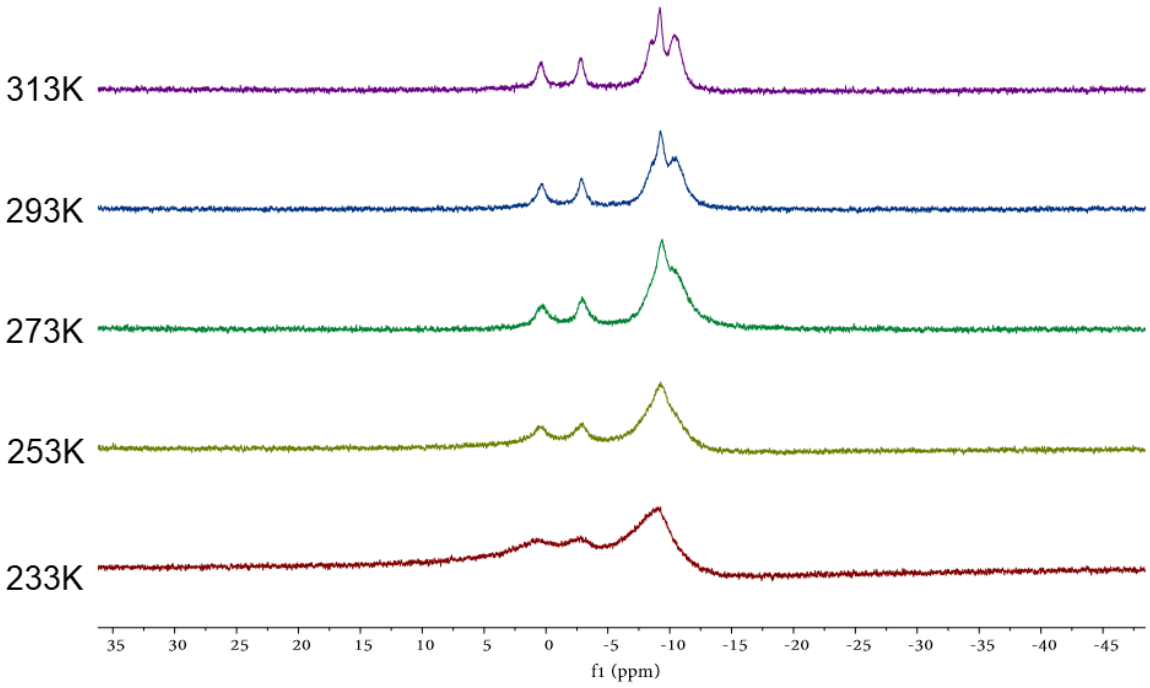


Fig. S22 ^{11}B NMR of **NAPH** from 313–233 K in $CDCl_3$

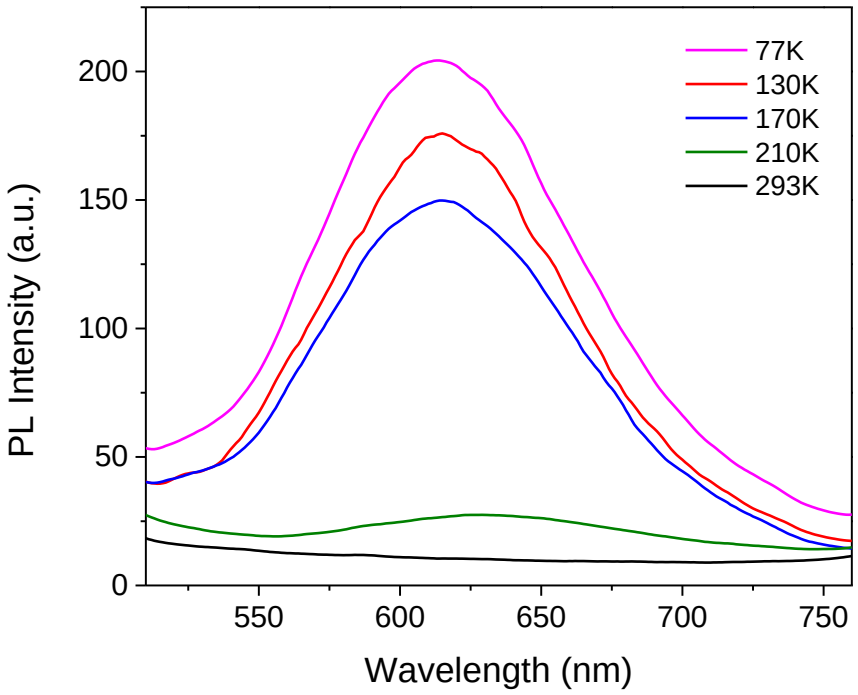


Fig. S23 PL spectra of **NAPH** from 293−77 K in DCM under excitation at 390 nm (c = 10^{-5} M).

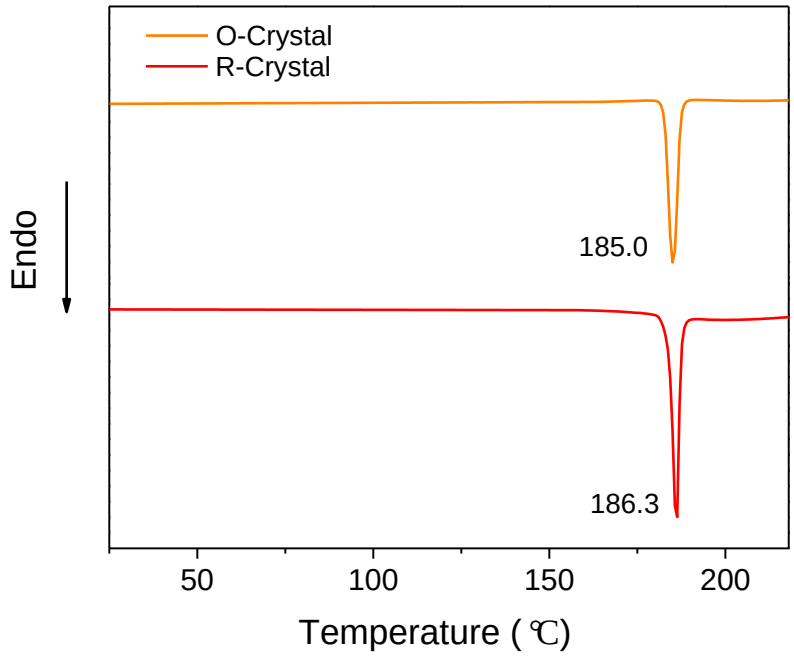


Fig. S24 DSC curves of **O-Crystal** and **R-Crystal** under nitrogen.

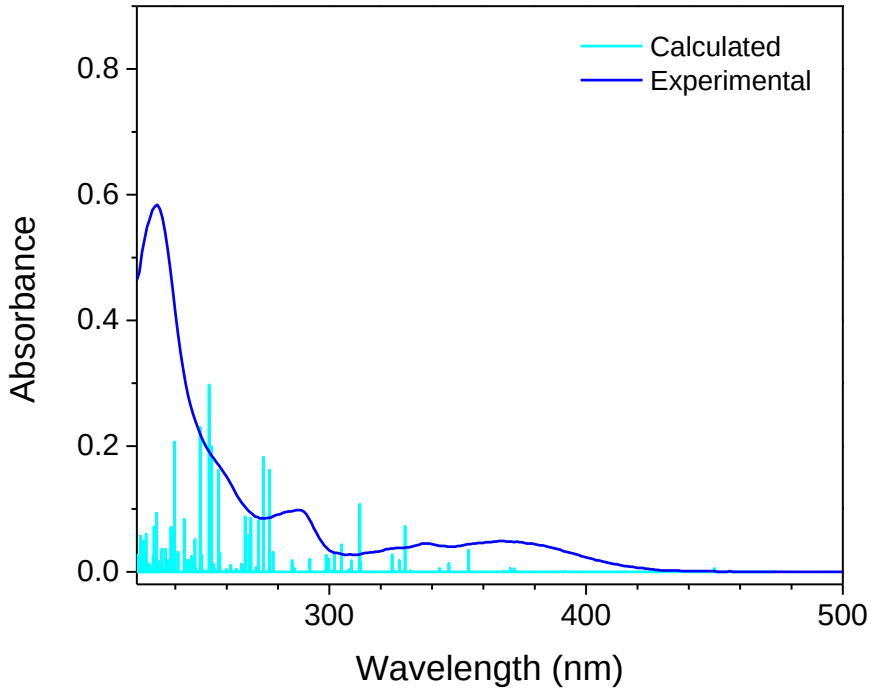


Fig. S25 Calculated and experimental (in DCM) UV-Vis absorption spectra of **NAPH**.

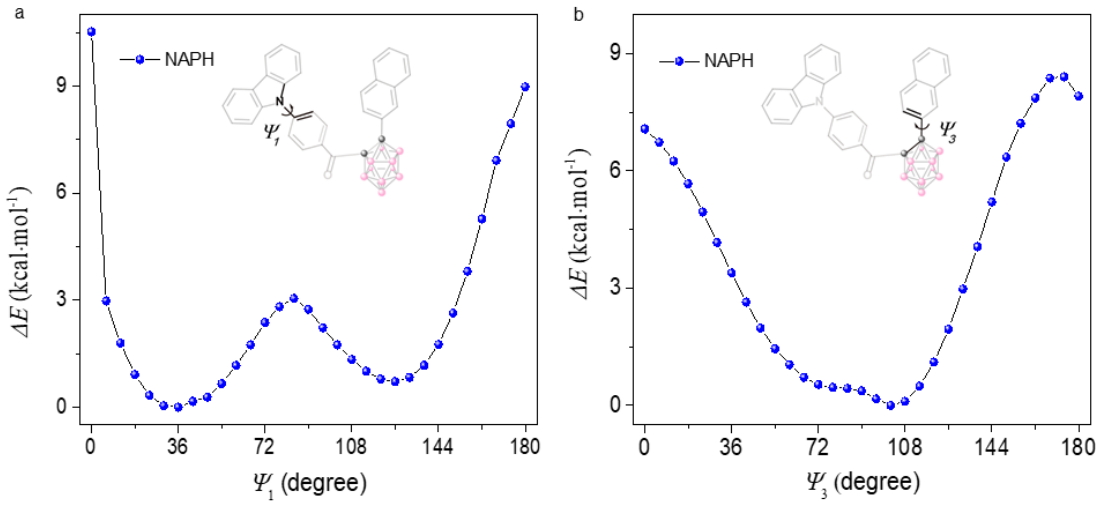


Fig. S26 Relative energy diagrams (ΔE/kcal·mol^{-1}) for NAPH in the S_0-state: relative energies as a function of dihedral angle (a) Ψ_1 and (b) Ψ_3 in its S_0-state (E = 0 kcal·mol^{-1} of optimized structure when Ψ = 36 °for Ψ_1 and Ψ=102 °for Ψ_3).

IV Supplementary Tables

Table S1. The photoluminensce wavelengths, decay dynamic parameters, quantum yields (Φ_{PL}), radiative rates (k_r), and non-radiative rates (k_{nr}) of **NAPH** for different aggregates. $k_r = \Phi_{PL}/\tau$; $k_{nr} = (1-\Phi_{PL})/\tau$.

	λ_{PL} (nm)	A_1/A_2	τ_1/τ_2 (ns)	$<\tau>$ (ns)	Φ_{PL}(%)	k_r ($10^7 s^{-1}$)	k_{nr} ($10^7 s^{-1}$)
O-Crystal	573	0.49/0.51	32.8/73.5	53.6	26.30	0.49	1.38
R-Crystal	634	0.91/0.09	4.9/13.3	5.7	5.47	0.96	16.70
Film	608	0.59/0.41	7.2/25.7	14.8	6.89	0.47	6.76

Table S2 Summary of crystallographic and structure refinement details for **NAPH**.

Compounds	**O-Crystal**	**R-Crystal**
Empirical formula	$C_{31}H_{29}B_{10}NO$	$C_{31}H_{29}B_{10}NO$
CCDC No.	2052180	2052181
Molecular weight	539.65	539.65
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a (Å)	8.9184(18)	12.2720(8)
b (Å)	11.079(2)	28.4854(18)
c (Å)	15.575(3)	8.7147(5)
α (°)	77.613(7)	90
β (°)	73.371(9)	107.071(2)
γ (°)	89.179(9)	90
V (Å^3)	1438.4(5)	2912.2(3)
Z	2	4
D_c (g cm^{-3})	1.246	1.231
μ (mm^{-1}) absort.coeff	0.328	0.068
F (000)	560.0	1120.0
Reflections collected / unique	13982/5726 [$R_{(int)}$ = 0.0162]	6670/6670 [$R_{(int)}$ = 0.0487]
Completeness	97%	99%

Data/restr./paras	5726/0/388	6670/0/389
Goodness-of-fit on F^2	1.052	1.031
R_1, wR_2(all data)	R_1 = 0.0658, wR_2 = 0.1127	R_1 = 0.0965, wR_2 = 0.1690
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0551, wR_2 = 0.1091	R_1 = 0.0618, wR_2 = 0.1446
Larg.peak/hole(e. Å)	0.36/-0.17	0.24/-0.24

Table S3 Singlet excitation energies (vertical transition), oscillator strength (*f*), and transition configurations of **NAPH** calculated by TD-DFT at the PBE0-D3(BJ)/def2TZVP.

Form	State	main configuration	*f*	E (eV)
O-Crystal	1	HOMO → LUMO (69.96%)	0.1783	3.1673
	2	HOMO-1 → LUMO (70.16%)	0.0001	3.5978
	3	HOMO → LUMO+1 (70.34%)	0.0091	3.6587
	4	HOMO-2 → LUMO (70.15%)	0.0038	3.7811
	5	HOMO-16 → LUMO (-11.03%) HOMO-9 → LUMO (-15.62%) HOMO-8 → LUMO (48.92%) HOMO-6 → LUMO (41.30%) HOMO-4 → LUMO (-10.48%)	0.0017	3.9082
R-Crystal	1	HOMO → LUMO (70.02%)	0.1717	3.1393
	2	HOMO-1 → LUMO (70.17%)	0.0002	3.5511
	3	HOMO → LUMO+1 (70.44%)	0.0104	3.6438
	4	HOMO-8 → LUMO (11.57%) HOMO-6 → LUMO (10.62%) HOMO-4 → LUMO (68.21%)	0.0016	3.7680
	5	HOMO-16 → LUMO (-10.46%) HOMO-9 → LUMO (19.27%) HOMO-8 → LUMO (44.99%) HOMO-6 → LUMO (40.29%) HOMO-4 → LUMO (-17.11%)	0.0012	3.9144

Table S4 Cartesian coordinates of **NAPH** at Ψ_1=36° from PBE0-D3(BJ) calculations (in Å).

Atom	x	y	z	H	-1.1726	-0.6542	-1.6229	H	-3.1536	3.1107	-0.9504
C	-3.5096	0.3923	-0.7352	C	4.4521	-3.6472	-1.152	C	-1.0961	3.2234	-1.5106
N	2.7939	-0.4908	0.9878	H	4.9297	-4.4478	-1.7205	H	-1.0815	4.3160	-1.4923
O	-3.0194	1.7803	2.4802	C	6.2297	0.4359	0.4186	B	-6.0470	-1.2321	0.5329
C	-0.7716	-0.8858	1.8936	H	7.0941	-0.0196	-0.0698	H	-6.9661	-1.8274	1.0227
H	-1.4652	-1.686	2.1557	C	0.0500	1.1003	-1.8905	B	-5.0411	0.5883	-1.4553

C	3.1919	-1.6406	0.3034	C	0.0984	2.5249	-1.8182	H	-5.1045	1.3449	-2.3811
C	5.0006	-0.2296	0.4437	C	2.4523	-2.7658	-0.0695	C	1.2393	0.3820	-2.1754
C	0.5746	-1.1795	1.7142	H	1.3980	-2.8681	0.1881	H	1.2018	-0.7075	-2.2294
H	0.9366	-2.1988	1.8533	C	5.2290	2.2513	1.6771	B	-5.8749	-0.9653	-1.2170
C	-3.6853	0.1401	0.9113	H	5.3362	3.2213	2.1680	H	-6.6668	-1.3649	-2.0248
C	1.4723	-0.1724	1.3355	B	-4.7527	-2.0591	-0.3712	B	-5.3238	0.1536	1.3692
C	3.8878	0.3696	1.0796	H	-4.7097	-3.2447	-0.5473	H	-5.5834	0.6073	2.4435
C	-2.6551	0.8378	1.8268	B	-4.7139	1.2653	0.1413	C	3.0993	-3.7597	-0.7983
C	-0.3023	1.4519	1.5137	H	-4.5341	2.4176	0.3733	H	2.5370	-4.6469	-1.0984
H	-0.6577	2.4804	1.4312	C	-1.2278	0.4301	1.7638	C	1.3403	3.1797	-2.0202
C	4.5554	-1.5107	-0.0561	C	6.3352	1.6793	1.0302	H	1.3772	4.2707	-1.9648
C	-2.2891	1.1317	-1.2053	H	7.2878	2.2127	1.0183	C	2.4844	2.4527	-2.2587
C	5.1844	-2.5244	-0.7847	C	3.9959	1.6082	1.7162	H	3.4403	2.9652	-2.3884
H	6.2359	-2.4296	-1.0649	H	3.1506	2.0563	2.2397	C	2.4344	1.0408	-2.3379
B	-3.2614	-1.1780	-0.0954	B	-4.1441	-0.9307	-1.6005	H	3.3489	0.4714	-2.5185
H	-2.1550	-1.6057	-0.0588	H	-3.5941	-1.2170	-2.6243	B	-6.2240	0.4080	-0.1413
C	1.0270	1.1533	1.2620	B	-4.4153	-1.3591	1.2302	H	-7.2563	1.0179	-0.1502
H	1.7155	1.9390	0.9490	H	-4.0575	-1.9527	2.2081				
C	-1.1620	0.4354	-1.5923	C	-2.2551	2.5509	-1.2074				

Table S5 Cartesian coordinates of **NAPH** at Ψ_2=84° from PBE0-D3(BJ) calculations (in Å).

Atom	x	y	z	H	-2.0719	1.5124	-1.6718	H	-3.8775	1.4532	2.2388
C	-3.9011	0.1758	-0.2089	C	6.0570	-4.377	-0.0711	C	-2.3270	2.8901	1.9466
N	3.1629	-1.4105	0.1667	H	6.8517	-5.1223	-0.1437	H	-2.4055	3.2796	2.9647
O	-2.7031	-1.1501	2.5945	C	6.2008	0.3003	-0.7355	B	-5.4785	-2.5497	-1.0714
C	-0.4262	-2.3139	0.1255	H	7.2352	0.0098	-0.9329	H	-6.0378	-3.5676	-1.3716
H	-1.0827	-3.022	-0.3802	C	-1.2967	2.9541	-0.2679	B	-5.5918	0.2573	-0.4458
C	3.9994	-2.5247	0.1144	C	-1.3724	3.4574	1.0662	H	-6.1112	1.3178	-0.2500
C	5.2504	-0.6648	-0.3905	C	3.7185	-3.8639	0.3928	C	-0.3605	3.5234	-1.1695
C	0.9323	-2.3215	-0.1634	H	2.7209	-4.1875	0.6922	H	-0.3037	3.1325	-2.1884
H	1.3303	-3.0100	-0.9101	C	4.4747	1.9973	-0.5912	B	-5.9464	-0.9533	-1.7016
C	-3.4773	-1.3218	0.3701	H	4.1805	3.0456	-0.6784	H	-6.8510	-0.7868	-2.4719
C	1.7957	-1.4241	0.4780	B	-4.4035	-1.6870	-2.2032	B	-4.8381	-2.3219	0.5666
C	3.9133	-0.2746	-0.1361	H	-4.1684	-2.056	-3.3199	H	-4.8219	-3.0878	1.4842
C	-2.3747	-1.3246	1.4484	B	-4.9231	-0.5998	0.9416	C	4.7622	-4.7787	0.2905
C	-0.0691	-0.5447	1.7317	H	-4.9445	-0.2033	2.0610	H	4.5660	-5.8324	0.5022
H	-0.4736	0.1349	2.4834	C	-0.9436	-1.4132	1.0638	C	-0.5020	4.5078	1.4540
C	5.3055	-2.1006	-0.2295	C	5.8082	1.6305	-0.8270	H	-0.559	4.8909	2.4760
C	-3.0607	1.3441	0.2261	H	6.5401	2.3968	-1.0912	C	0.3927	5.0425	0.5562
C	6.3365	-3.0395	-0.3255	C	3.5079	1.0567	-0.2491	H	1.0536	5.8562	0.8645
H	7.3477	-2.7228	-0.591	H	2.4724	1.3602	-0.0901	C	0.4628	4.5482	-0.7678
B	-3.1282	-0.9379	-1.2606	B	-4.4848	0.0427	-1.8078	H	1.1807	4.9784	-1.4694
H	-2.0042	-0.7071	-1.5682	H	-4.2568	0.9530	-2.5506	B	-6.2155	-1.3427	0.0124
C	1.2849	-0.5394	1.4363	B	-3.7235	-2.5346	-0.7943	H	-7.2997	-1.466	0.5089

H	1.9615	0.1385	1.9583	H	-2.9568	-3.4551	-0.8118
C	-2.1511	1.8949	-0.6536	C	-3.1526	1.8699	1.5413

Table S6 Cartesian coordinates of **NAPH** at Ψ_3=102° from PBE0-D3(BJ) calculations (in Å).

Atom	x	y	z	H	-1.8171	1.1856	-1.8692	H	-3.6780	1.6350	1.9895
C	-3.7723	0.1436	-0.3318	C	6.3005	-3.4849	-0.4552	C	-2.0117	2.9107	1.6008
N	3.1595	-0.8259	0.0868	H	7.1566	-4.1458	-0.6053	H	-2.0730	3.3987	2.5766
O	-2.6697	-1.3186	2.5714	C	6.0084	1.2256	-0.7152	B	-5.5587	-2.5053	-1.0033
C	-0.3347	-2.0415	-0.0083	H	7.0594	1.0487	-0.9550	H	-6.1959	-3.4956	-1.2312
H	-0.934	-2.7562	-0.5725	C	-0.9485	2.6862	-0.5876	B	-5.4536	0.3380	-0.5659
C	4.0907	-1.8505	-0.0756	C	-1.0020	3.3164	0.6925	H	-5.8892	1.4456	-0.439
C	5.1573	0.1520	-0.4385	C	3.9373	-3.2285	0.0898	C	0.0414	3.0948	-1.5187
C	1.0144	-1.9011	-0.3062	H	2.9800	-3.6659	0.3760	H	0.0805	2.6077	-2.4961
H	1.4606	-2.4805	-1.1157	C	4.1410	2.7394	-0.3955	B	-5.9104	-0.9235	-1.7365
C	-3.4561	-1.3394	0.3440	H	3.7520	3.7598	-0.3867	H	-6.8078	-0.7401	-2.5113
C	1.8043	-0.9911	0.4080	B	-4.4325	-1.8041	-2.1950	B	-4.8874	-2.2187	0.6137
C	3.7972	0.3953	-0.1294	H	-4.2367	-2.2636	-3.2853	H	-4.9202	-2.9211	1.5803
C	-2.3435	-1.3526	1.4119	B	-4.8386	-0.4734	0.8731	C	5.0559	-4.0323	-0.1088
C	-0.1111	-0.4000	1.7506	H	-4.8189	-0.0019	1.9634	H	4.9598	-5.1136	0.0136
H	-0.563	0.1702	2.5639	C	-0.9153	-1.2794	1.0122	C	-0.0562	4.3275	0.9997
C	5.3449	-1.2811	-0.4029	C	5.4958	2.5173	-0.6846	H	-0.0961	4.8078	1.9805
C	-2.8434	1.2741	0.0141	H	6.1492	3.3670	-0.8942	C	0.8899	4.7050	0.0750
C	6.4530	-2.1106	-0.5971	C	3.2711	1.6888	-0.1201	H	1.6092	5.4900	0.3206
H	7.4251	-1.6816	-0.8506	H	2.2166	1.8817	0.0812	C	0.9375	4.086	-1.1965
B	-3.0958	-1.0929	-1.3104	B	-4.3800	-0.0505	-1.9159	H	1.6952	4.3926	-1.9207
H	-1.9605	-0.9687	-1.6374	H	-4.0922	0.7881	-2.7197	B	-6.191	-1.1767	0.0009
C	1.2324	-0.2463	1.4471	B	-3.8046	-2.6038	-0.7348	H	-7.2767	-1.1841	0.5094
H	1.8546	0.4396	2.0235	H	-3.1111	-3.5798	-0.6942				
C	-1.8793	1.6659	-0.8922	C	-2.9112	1.9256	1.2731				