Supporting Information

Molecular Dual-Functionalization Unlocks Room-Temperature Phosphorescence of Graphitic Carbon Nitride for Environmentally Robust Encryption

Jingyang Xu[1], Qikun Sun[2], Mingming Zhang[1,3], Xinyi Wang[1], Yingqin Xu[1], Kang Liu[1], Jixiang Xu[1], Fangxu Dai[1,4,*], Lei Wang[1], Jun Xing[1,*]

[1]State Key Laboratory of Advanced Optical Polymer and Manufacturing Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042, China.

[2]School of Polymer Science and Engineering, Qingdao University of Science & Technology, Qingdao, 266042, China.

[3]College of Sino-German Science and Technology, Qingdao University of Science & Technology, Qingdao 266042, China.

[4]School of Pharmacy, Jining Medical University, Rizhao 276800, China.

*Correspondence: daifangxu@mail.jnmc.edu.cn (F.D.), xingjun@qust.edu.cn (J.X.)

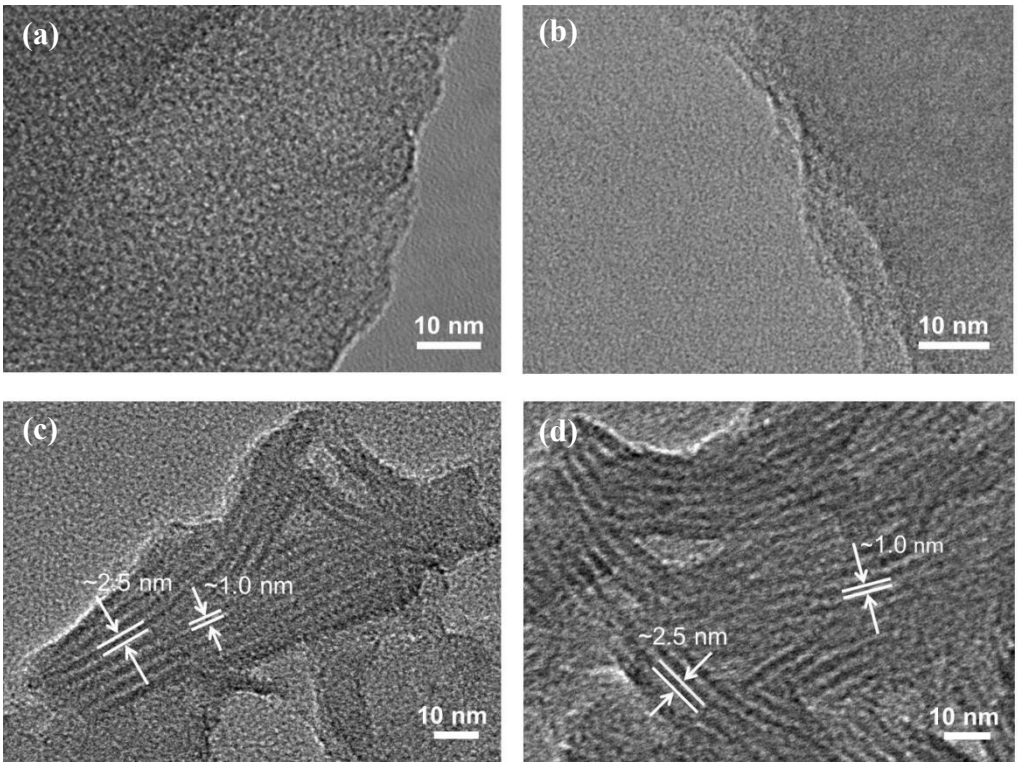

Figure S1. High-resolution TEM images of layered structures of the PhCN (a) and Np-PhCN (b). High-resolution TEM images of banded structures of the PhCN (c) and Np-PhCN (d).

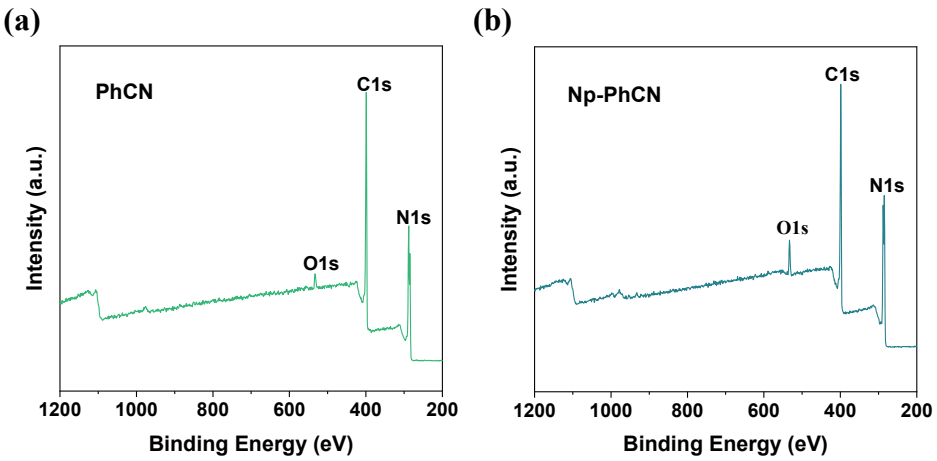

Figure S2. XPS spectra of the PhCN (a) and Np-PhCN (b) samples. The presence of the element O is mainly due to the material being exposed to the air and absorbing CO_2.

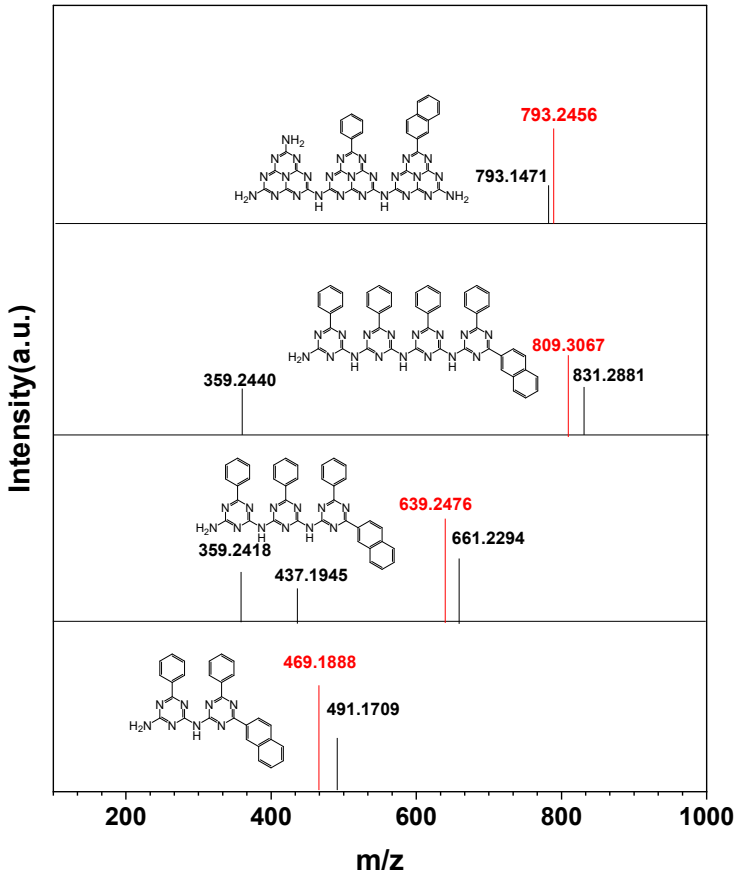

Figure S3. LC-MS data for the washing solution of the synthesized sample Np-PhCN.

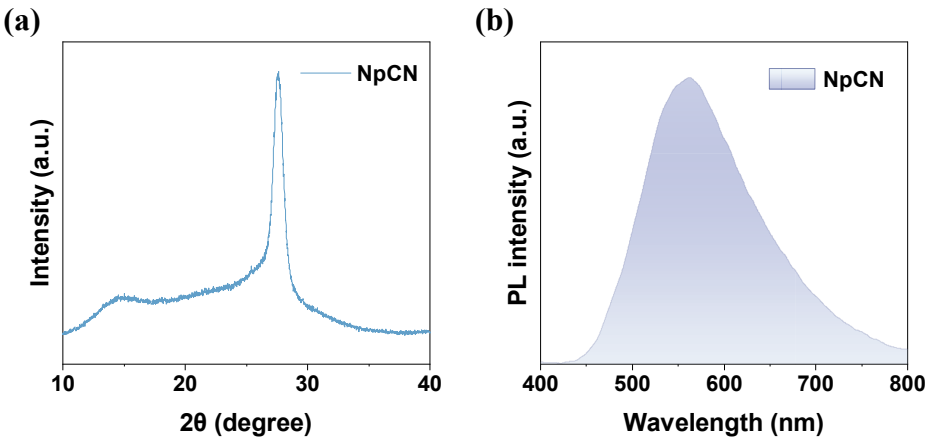

Figure S4. XRD patterns and emission spectra of NpCN. The XRD pattern of NpCN has the diffraction peak at 27.6°, which corresponds to the (002) graphite-like plane of conjugated aromatic systems. The NpCN exhibits weak fluorescence emission and an absence of phosphorescence.

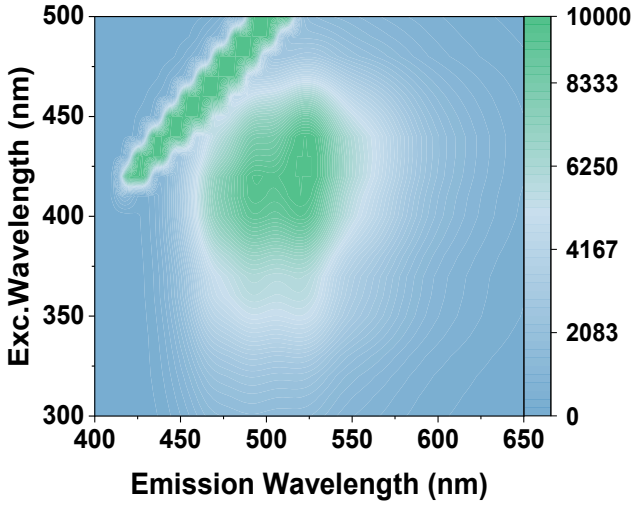

Figure S5. The fluorescence excitation spectrum of PhCN.

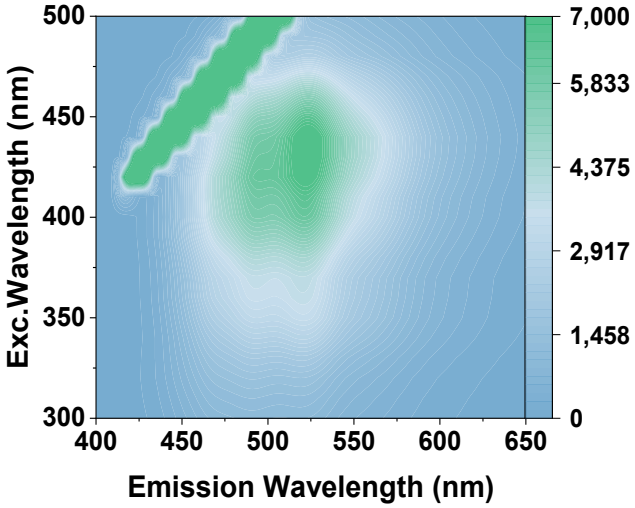

Figure S6. The fluorescence excitation spectrum of Np-PhCN.

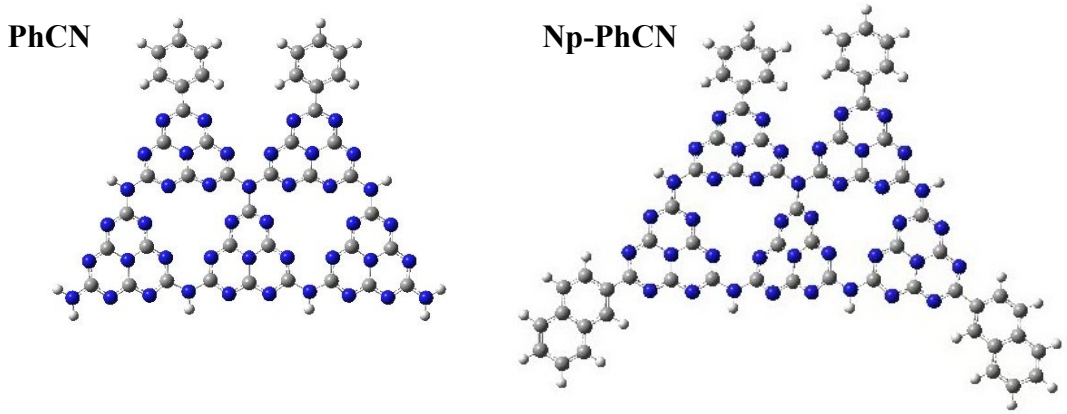

Figure S7. Theoretically optimized structure of PhCN and Np-PhCN.

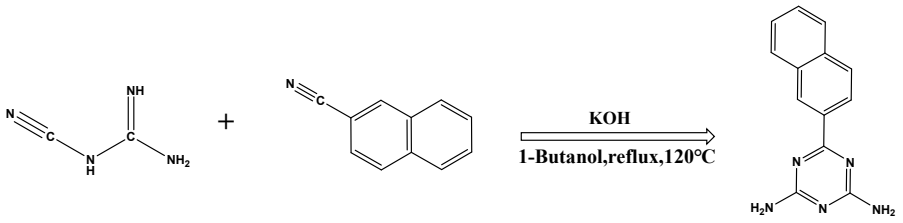

Figure S8. The synthesis mechanism of 2,4-diamino-6-naphthyl-1,3,5-triazine.

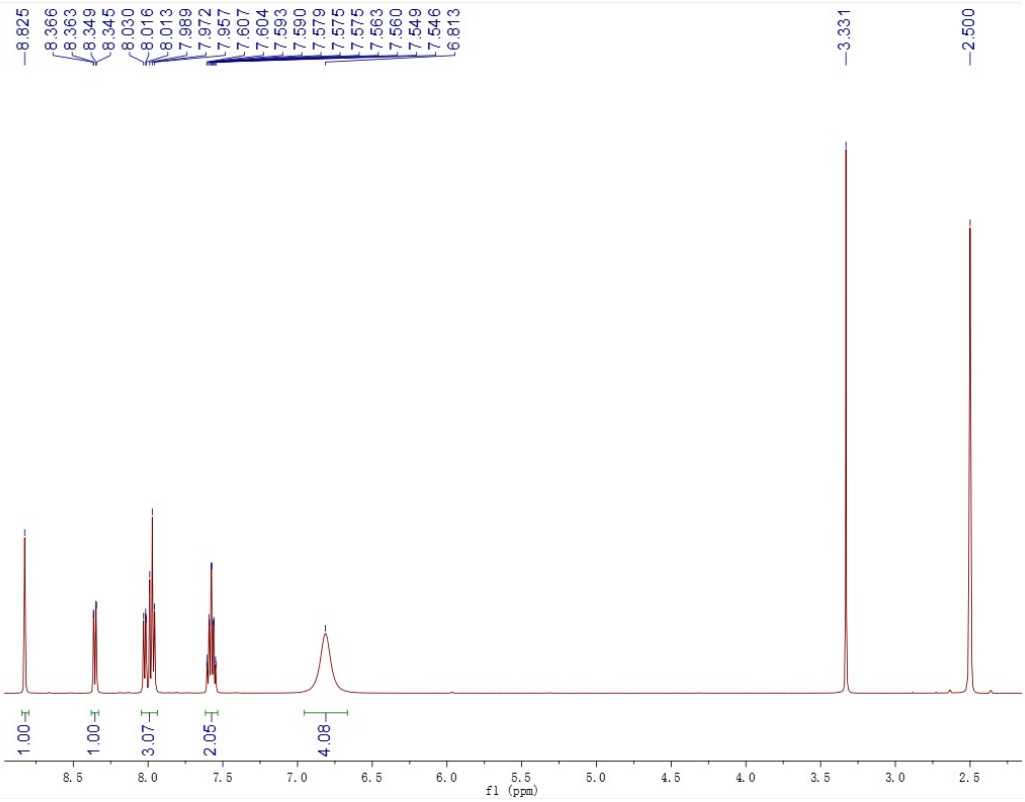

Figure S9. ^{1}H NMR of the synthesized 2,4-diamino-6-naphthyl-1,3,5-triazine. The ^{1}H NMR spectrum shows that the peak at 6-9 ppm is the characteristic peak of 2,4-diamino-6-naphthyl-1,3,5-triazine. The peaks at 2.500 and 3.331 ppm are derived from absorbed water in sample and the solvent DMSO.

Table S1. The fitting data of C 1s XPS spectra of PhCN and Np-PhCN.

Samples	Peak fit	Peak BE (eV)	FWHM (eV)	Content (%)
PhCN	C-C/C=C	284.7	1.1	33.4
	C-Ph	286.1	2.0	15.5
	N-C=N	288.3	1.4	51.1
Np-PhCN	C-C/C=C	284.8	1.2	45.1
	C-Ph/C-Np	286.3	1.8	12.2
	N-C=N	288.2	1.1	42.5

Table S2. The fitting data of N 1s XPS spectra of PhCN and Np-PhCN.

Samples	Peak fit	Peak BE (eV)	FWHM (eV)	Content (%)
PhCN	N_{2C}	398.8	1.2	54.9
	NH_x	400.0	1.3	25.4
	N_{3C}	401.1	1.3	15.8
	π-excitation	405.0	3.1	3.8
Np-PhCN	N_{2C}	398.7	1.2	68.7
	NH_x	399.7	1.1	15.8
	N_{3C}	401.1	1.1	11.4
	π-excitation	404.4	2.0	3.8

Table S3. XPS elemental content analysis of PhCN.

Elements	FWHM (eV)	Atomic content (%)
C 1s	5.71	59.42
N 1s	2.85	38.93
O 1s	3.75	1.65

Table S4. XPS elemental content analysis of Np-PhCN.

Elements	FWHM (eV)	Atomic content (%)
C 1s	5.55	60.76
N 1s	2.80	33.58
O 1s	3.28	3.82

Table S5. The fluorescence peak locations and PLQYs of g-CN.

Sample	Peak center (nm)	PLQY (%)	PQY(%)
p-CN	465	9	/
PhCN	520	41	/
NpCN	560	3	/
Np-PhCN	520	37	4.4

Table S6. The fitting data of temperature-dependent phosphorescence lifetime for Np-PhCN.

Temperature	τ_1 (ms)	τ_2 (ms)	τ_3 (ms)
77 K	7.7	87	1130
160 K	5.8	53	770
230 K	4.1	28	284
300 K	3.4	16	85
370 K	3.1	12	99

Table S7. Cartesian coordinate system of PhCN.

Element	X	Y	Z
N	5.94337	2.4938	0.02101
C	5.76425	1.24521	-0.4544
N	4.59244	0.67611	-0.78683
C	3.47586	1.28552	-0.39591
N	3.57813	2.54428	0.25492
C	4.84648	3.17697	0.37586
N	2.26029	0.75537	-0.57376
C	1.22948	1.35376	0.03515
N	1.24603	2.52153	0.69398
C	2.41015	3.18035	0.7569
N	2.52516	4.40107	1.28424
C	3.74562	4.98468	1.30498
N	4.89594	4.4128	0.87854
C	3.83005	6.34728	1.84251
N	6.91558	0.49245	-0.62395
C	5.07026	7.00262	1.90194
C	5.14557	8.29642	2.40937
C	3.98794	8.94104	2.8593
C	2.75151	8.28855	2.80123
C	2.66922	6.99476	2.29472
N	-1.24594	2.52161	-0.69399
C	-1.22947	1.3538	-0.03523
N	-2.26036	0.7554	0.57357
C	-3.47589	1.28559	0.39566
N	-3.57809	2.54439	-0.25513
C	-2.41004	3.18047	-0.7569
N	-4.59254	0.67618	0.7864
C	-5.76431	1.24533	0.45392
N	-5.94335	2.49394	-0.02146
C	-4.84642	3.1771	-0.3762
N	-4.8958	4.41297	-0.87879
C	-3.74541	4.98485	-1.30504
N	-2.52496	4.40125	-1.28416
C	-3.82972	6.34755	-1.84235
N	-6.91566	0.49263	0.62338
C	-2.66882	6.99505	-2.29436
C	-2.75101	8.28894	-2.80065
C	-3.98739	8.9415	-2.8587
C	-5.14509	8.29686	-2.40898
C	-5.06989	7.00297	-1.90176
N	2.16402	-3.37294	0.93911

C	2.20691	-4.67501	0.61678
N	1.15204	-5.45101	0.26321
C	-0.00007	-4.82401	0.00022
N	-0.00005	-3.39716	0.00016
C	1.08598	-2.68839	0.5676
N	-1.15217	-5.45101	-0.26274
C	-2.20704	-4.67501	-0.61639
N	-2.1641	-3.37299	-0.93887
C	-1.08605	-2.68841	-0.5674
N	-0.99382	-1.35662	-0.66972
C	-0.00002	-0.75942	0.00004
N	0.99378	-1.35657	0.66981
N	3.43263	-5.31565	0.58221
N	-3.43275	-5.31564	-0.58184
N	-0.00002	0.65885	-0.00002
C	-4.66746	-4.70875	-0.40163
N	-5.6601	-5.52826	0.01326
C	-6.81441	-4.95215	0.38788
N	-6.89809	-3.52529	0.39231
C	-5.82672	-2.76399	-0.13045
N	-4.74496	-3.38978	-0.58059
N	-7.87543	-5.64856	0.7807
C	-8.97048	-4.95058	1.18416
N	-9.09706	-3.59687	1.26909
C	-8.06178	-2.86188	0.88432
N	-8.05187	-1.51689	0.96031
C	-6.95932	-0.88432	0.49595
N	-5.91012	-1.44147	-0.12629
N	-10.03822	-5.67174	1.55036
C	4.66729	-4.70878	0.40173
N	4.74481	-3.38979	0.58047
C	5.82655	-2.76406	0.13022
N	6.8979	-3.52546	-0.39249
C	6.81423	-4.95231	-0.38776
N	5.65992	-5.52836	-0.01306
C	8.06161	-2.86213	-0.88454
N	9.09685	-3.5972	-1.26926
C	8.97025	-4.95089	-1.18413
N	7.87524	-5.64878	-0.78048
N	5.90996	-1.44155	0.12587
C	6.95918	-0.8845	-0.49641
N	8.05173	-1.51717	-0.96068
N	10.038	-5.67211	-1.55022
H	5.94729	6.47715	1.54839

H	6.10165	8.804	2.4567
H	4.04936	9.94858	3.25458
H	1.85695	8.79011	3.15061
H	1.7284	6.46388	2.23649
H	-7.79567	0.99083	0.73504
H	-1.72804	6.4641	-2.23615
H	-1.85639	8.79051	-3.14988
H	-4.04872	9.94911	-3.25382
H	-6.10114	8.80449	-2.4563
H	-5.94698	6.4775	-1.54836
H	3.40216	-6.31674	0.39319
H	-3.40231	-6.31671	-0.39266
H	-10.87303	-5.19347	1.86704
H	-9.9891	-6.68274	1.51269
H	9.98891	-6.6831	-1.51238
H	10.87279	-5.19387	-1.86701
H	7.79561	0.99059	-0.73572

Table S8. Cartesian coordinate system of Np-PhCN.

Element	X	Y	Z
N	5.90957	3.8395	0.64128
C	5.77976	2.59443	0.14565
N	4.64987	2.02434	-0.30609
C	3.49796	2.63329	-0.03243
N	3.53252	3.891	0.62693
C	4.78111	4.52338	0.88178
N	2.30811	2.10301	-0.33565
C	1.2193	2.70137	0.16326
N	1.16714	3.86821	0.82043
C	2.31875	4.52718	1.00522
N	2.37818	5.74657	1.5435
C	3.58982	6.32986	1.69451
N	4.77845	5.75676	1.38989
C	3.61864	7.6902	2.24115
N	6.94453	1.84008	0.09029
C	4.84671	8.34372	2.43218
C	4.86976	9.63574	2.94881
C	3.67193	10.2804	3.27717
C	2.44757	9.62991	3.08787
C	2.41728	8.33792	2.5714
N	-1.16711	3.86822	-0.82033
C	-1.2193	2.70139	-0.16312
N	-2.30811	2.10304	0.33578
C	-3.49795	2.63333	0.03255
N	-3.53251	3.89102	-0.62686
C	-2.31873	4.52716	-1.00517
N	-4.64986	2.02439	0.30621
C	-5.77976	2.59447	-0.14556
N	-5.90957	3.83952	-0.64125
C	-4.7811	4.52338	-0.88177
N	-4.77842	5.75673	-1.38995
C	-3.58979	6.32982	-1.69457
N	-2.37815	5.74655	-1.5435
C	-3.61861	7.69013	-2.24127
N	-6.94452	1.84012	-0.0902
C	-4.84668	8.34359	-2.43245
C	-4.86973	9.63559	-2.94913
C	-3.6719	10.2803	-3.27737
C	-2.44752	9.62986	-3.08792
C	-2.41723	8.3379	-2.5714

N	2.06075	-2.02593	1.14752
C	2.1338	-3.32784	0.83354
N	1.12028	-4.104	0.37641
C	-0.00001	-3.47711	-0.00006
N	-0.00002	-2.05013	0.00001
C	1.0245	-1.34089	0.67133
N	-1.1203	-4.10399	-0.37657
C	-2.13383	-3.3278	-0.83365
N	-2.06077	-2.02588	-1.14756
C	-1.02454	-1.34085	-0.67128
N	-0.92376	-0.00949	-0.76322
C	-0.00001	0.58852	0.00006
N	0.92373	-0.00952	0.76329
N	3.35793	-3.96925	0.92288
N	-3.35797	-3.96919	-0.92297
N	0	2.00588	0.00007
C	-4.60184	-3.36168	-0.87409
N	-5.63538	-4.17928	-0.5569
C	-6.8169	-3.59878	-0.303
N	-6.90141	-2.17495	-0.31343
C	-5.78316	-1.41507	-0.73077
N	-4.66306	-2.04415	-1.06898
N	-7.92228	-4.28854	-0.01405
C	-9.05649	-3.60724	0.27734
N	-9.17436	-2.25823	0.33741
C	-8.10476	-1.51127	0.05643
N	-8.10916	-0.17003	0.12818
C	-6.97318	0.46707	-0.22423
N	-5.86849	-0.0924	-0.73831
C	-10.25914	-4.39454	0.56171
C	4.60181	-3.36173	0.87403
N	4.66303	-2.04421	1.06894
C	5.78314	-1.41512	0.73079
N	6.9014	-2.175	0.31348
C	6.81688	-3.59883	0.303
N	5.63534	-4.17934	0.55685
C	8.10477	-1.51131	-0.05628
N	9.17438	-2.25826	-0.33726
C	9.05649	-3.60727	-0.27726
N	7.92227	-4.28857	0.01406
N	5.86848	-0.09246	0.73837
C	6.97318	0.46703	0.22435
N	8.10919	-0.17005	-0.128

C	10.25915	-4.39457	-0.56163
C	-10.20546	-5.7777	0.52004
C	-11.3575	-6.55436	0.78819
C	-12.58957	-5.88703	1.10642
C	-12.61024	-4.46195	1.14211
C	-11.48005	-3.73216	0.87827
C	-11.3319	-7.97756	0.75213
C	-12.468	-8.70668	1.01724
C	-13.68361	-8.04668	1.33118
C	-13.74282	-6.67095	1.37476
C	11.48009	-3.73218	-0.87802
C	12.61029	-4.46196	-1.14187
C	12.58958	-5.88704	-1.10636
C	11.35748	-6.55438	-0.7883
C	10.20543	-5.77774	-0.52014
C	13.74283	-6.67096	-1.37471
C	13.68359	-8.04669	-1.33131
C	12.46794	-8.7067	-1.01753
C	11.33184	-7.97759	-0.75242
H	5.75558	7.81837	2.17101
H	5.81608	10.14186	3.09773
H	3.69266	11.28654	3.68007
H	1.52199	10.13169	3.34345
H	1.48702	7.80873	2.41358
H	-7.8318	2.33721	-0.05599
H	-5.75556	7.81821	-2.17137
H	-5.81605	10.14167	-3.09817
H	-3.69262	11.28643	-3.68031
H	-1.52194	10.13168	-3.34342
H	-1.48697	7.80875	-2.41347
H	3.34687	-4.97056	0.73186
H	-3.3469	-4.97053	-0.73204
H	-9.26427	-6.25612	0.27876
H	-13.54194	-3.96216	1.38378
H	-11.4779	-2.65113	0.90221
H	-10.39843	-8.47451	0.51136
H	-12.44118	-9.78944	0.98795
H	-14.57008	-8.635	1.53769
H	-14.67256	-6.1667	1.61503
H	11.47797	-2.65114	-0.90182
H	13.54201	-3.96216	-1.38341
H	9.26421	-6.25616	-0.27899
H	14.6726	-6.16669	-1.61485

H	14.57006	-8.63501	-1.53783
H	12.4411	-9.78946	-0.98837
H	10.39834	-8.47455	-0.51177
H	7.83178	2.33718	0.0561

Table S9. The energy levels of PhCN and Np-PhCN.

PhCN energy level	S	T	Np-PhCN energy level	S	T
1	2.72 eV	2.56 eV	1	2.70 eV	2.32 eV
2		2.58 eV	2		2.55 eV
3		2.69 eV	3		2.56 eV
4		2.90 eV	4		2.63 eV
5		2.92 eV	5		2.69 eV
6		2.99 eV	6		2.75 eV
7			7		2.95 eV
8			8		2.98 eV
9			9		3.03 eV