**Effects of the lateral substituent on the cubic
phase formation of two analogous
compounds,
4'-*n*-hexadecyloxy-3'-cyanobiphenyl-4-carbo
xylic acid (ACBC-16) and its 3'-nitro
compound (ANBC-16)**

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**Supplementary Materials
(15 Pages)**

Quantum calculation

Stable conformations of cyanoPBA and nitroPBA were determined at the DFT/B3LYP/6-31G* level. The Cartesian coordinates of the stationary points in the ground states optimized are tabulated. Values are given in Å.

1. Stable conformations of cyanoPBA and nitroPBA

Energies of anti and syn form for cyanoPBA and nitroPBA (Figure S1) are shown in Table S1. For both cyanoPBA and nitroPBA, the syn form is certainly stable, although the energy difference between the anti and syn forms is very small.

Figure S1: anti and syn form of cyanoPBA and nitroPBA

Table S1: Energies of anti/syn form of cyanoPBA and nitroPBA calculated by DFT/B3LYP/6-31G*

	anti	syn	$E(\text{anti} - \text{syn}) / \text{kJ mol}^{-1}$
cyanoPBA	-744.12209	-744.12217	0.210
nitroPBA	-856.38038	-856.38048	0.262

2. Cartesian coordinates, main geometric parameters, and frequencies of cyanoPBA

Table S2: Cartesian coordinate of optimized structure of syn cyanoPBA monomer

Atoms			
C	-0.13614	0.302164	-0.06209
C	-0.98328	1.285524	0.479375
C	-2.35886	1.095092	0.523418
C	-2.92503	-0.08593	0.026233
C	-2.09202	-1.07379	-0.51569
C	-0.71527	-0.87862	-0.55807
H	-0.55562	2.193814	0.8937
H	-3.01395	1.848255	0.948617
H	-2.52541	-1.98626	-0.90969
H	-0.08295	-1.6398	-1.00562
C	-4.40161	-0.23776	0.097213
O	-5.16403	0.589368	0.556023
O	-4.83894	-1.41835	-0.41166
H	-5.80882	-1.40512	-0.31206
C	1.333709	0.50763	-0.1087
C	2.21309	-0.55632	0.132975
C	1.879606	1.771211	-0.39506
C	3.601321	-0.36154	0.08794
H	1.825116	-1.53832	0.382412
C	3.25941	1.966697	-0.43998
H	1.21409	2.602315	-0.60885
C	4.129977	0.907126	-0.20033
H	5.205136	1.048822	-0.23339
C	4.482644	-1.4643	0.346027
N	5.197561	-2.35787	0.554526
H	3.657893	2.950169	-0.67141

Table S3: Cartesian coordinate of optimized structure of anti cyanoPBA monomer

Atoms			
C	-0.13627	0.278633	-0.0731
C	-0.69955	-0.90835	-0.57458
C	-2.07293	-1.11594	-0.53759
C	-2.92103	-0.14019	0.002181
C	-2.37239	1.047001	0.505209
C	-0.99677	1.250261	0.466593
H	-0.05686	-1.66152	-1.0208
H	-2.51091	-2.02718	-0.9312
H	-3.02347	1.801484	0.932356
H	-0.58084	2.162072	0.885135
C	-4.3819	-0.41216	0.015685
O	-4.90459	-1.42385	-0.40748
O	-5.10606	0.600555	0.558681
H	-6.03645	0.312013	0.514105
C	1.331313	0.501303	-0.11186
C	1.864304	1.771513	-0.39324
C	2.221387	-0.55327	0.131873
C	3.241994	1.982683	-0.43068
H	1.190499	2.595316	-0.60927
C	3.607575	-0.34276	0.094386
H	1.843259	-1.54023	0.376752
C	4.123204	0.932503	-0.18858
H	3.630586	2.970881	-0.65836
H	5.196848	1.086335	-0.216
C	4.500413	-1.43565	0.354696
N	5.225193	-2.3209	0.56452

Table S4: Cartesian coordinate of optimized structure of cyanoPBA dimer

Atoms			
C	-6.22948	-0.31615	-0.19582
C	-5.43204	-1.47447	-0.19766
C	-4.04538	-1.38525	-0.197
C	-3.41853	-0.13228	-0.19437
C	-4.20195	1.029675	-0.1917
C	-5.5895	0.935533	-0.19269
H	-5.90483	-2.45185	-0.17143
H	-3.43017	-2.27867	-0.18949
H	-3.71882	2.000265	-0.19767
H	-6.18528	1.843212	-0.21833
C	-1.93389	-0.07273	-0.19455
O	-1.23989	-1.09402	-0.19655
O	-1.43798	1.154416	-0.19309
H	-0.434	1.11875	-0.19417
H	5.904759	2.451812	-0.17151
C	5.432003	1.474413	-0.1977
C	6.229484	0.316131	-0.19584
C	4.045345	1.38513	-0.19705
C	5.589574	-0.93559	-0.19275
C	3.418556	0.132131	-0.19442
H	3.430092	2.278523	-0.18954
C	4.202031	-1.0298	-0.19174
H	6.18541	-1.84323	-0.2184
C	1.933923	0.07251	-0.19459
H	3.718946	-2.00041	-0.19774
O	1.239866	1.093763	-0.19658
O	1.438073	-1.15466	-0.19312
H	0.434105	-1.11902	-0.1942
C	7.711083	0.414428	-0.19771
C	8.488838	-0.48065	0.549022
C	8.369671	1.405851	-0.94598
C	9.888247	-0.38646	0.546758
H	8.011355	-1.24159	1.157369
C	9.760697	1.500957	-0.9493

H	7.784975	2.092597	-1.55073
C	10.53026	0.609883	-0.20647
H	11.61323	0.675224	-0.20281
C	-7.71107	-0.41437	-0.19764
C	-8.48882	0.480803	0.549009
C	-8.36971	-1.40575	-0.94588
C	-9.88824	0.386665	0.546736
H	-8.01131	1.241762	1.15732
C	-9.76073	-1.50083	-0.94925
H	-7.78505	-2.09253	-1.55065
C	-10.5302	-0.60968	-0.20644
H	-11.6132	-0.67499	-0.20282
C	-10.6643	1.309658	1.324768
N	-11.2941	2.057789	1.954543
H	-10.2476	-2.26983	-1.54163
H	10.24759	2.269993	-1.54171
C	10.66423	-1.30939	1.324872
N	11.29391	-2.05755	1.954771

Table S5: Geometric parameters of cyanoPBA monomer and dimer optimized at the DFT/B3LYP/6-31G* level

	monomer	dimer
	Bond lengths / Å	
C–C (Phenyl) ¹	1.4	1.4
C–C (Benzoic acid) ²	1.399	1.399
O–H (calboxyl)	0.9075	1.399
O–H (carboxyl)	–	1.6742
	Angle / degree	
benzene-benzene ³	38.1	38.2

¹ Averaged C–C bond length of phenyl group

² Averaged C–C bond length of benzoic acid

³ The distortion degree between benzene rings

Table S6: Frequencies calculated at the DFT/B3LYP/6-31G* level for cyanoPBA dimer

Frequencies / cm ⁻¹					
4.529	318.8104	707.1696	985.7091	1321.449	1655.205
15.768	379.0733	707.7859	992.2421	1321.473	1667.929
20.7603	384.2991	712.0577	992.2739	1327.592	1668.278
27.3037	398.0569	714.7674	995.8871	1330.215	1721.029
45.0358	398.3024	717.2026	995.9968	1344.209	1765.473
48.7106	420.4653	723.6644	1015.561	1344.333	2350.162
51.2596	420.567	779.7014	1015.578	1355.818	2350.181
63.9461	460.9934	779.8041	1036.006	1356.825	3087.938
75.2731	462.5202	805.8281	1036.482	1367.088	3183.202
79.897	463.7544	816.2642	1071.672	1367.329	3198.001
82.672	477.8243	819.0615	1071.74	1437.872	3198.092
89.4927	485.1242	819.134	1128.424	1437.888	3202.04
92.1097	488.2656	863.2342	1128.471	1468.743	3202.176
112.9549	526.1467	863.3834	1146.943	1471.556	3202.769
134.8618	530.3495	867.8709	1146.952	1477.832	3202.935
140.6695	531.2097	868.0974	1159.267	1511.667	3213.331
156.5002	555.7492	879.8336	1162.723	1528.235	3213.379
158.2013	578.6702	880.155	1206.612	1528.283	3221.512
190.1251	579.3816	917.5849	1206.625	1561.357	3221.597
194.9441	630.9646	929.1219	1210.704	1561.686	3226.373
242.7614	631.1263	929.1529	1210.724	1613.395	3226.462
248.2734	652.1427	938.8175	1221.081	1614.521	3230.439
265.179	652.54	938.907	1222.378	1633.214	3230.449
280.7486	660.3562	965.4137	1313.517	1633.311	3236.803

3. Cartesian coordinates, main geometric parameters, and frequencies of nitroPBA

Tabel S7: Cartesian coordinate of optimized structure of syn cyanoPBA monomer

Atoms			
C	0.516073	0.409034	0.074458
C	1.399523	1.345422	-0.49163
C	2.765711	1.096943	-0.53944
C	3.285327	-0.09648	-0.02164
C	2.41557	-1.03799	0.544501
C	1.048459	-0.78495	0.5906
H	1.007988	2.262113	-0.92282
H	3.448794	1.8133	-0.98373
H	2.813024	-1.9601	0.953574
H	0.387628	-1.51115	1.054628
C	4.753928	-0.31154	-0.09844
O	5.546982	0.474398	-0.57722
O	5.144621	-1.4997	0.429919
H	6.113502	-1.52954	0.324247
C	-0.94387	0.674756	0.124995
C	-1.8662	-0.3619	-0.07549
C	-1.43955	1.967645	0.373626
C	-3.22875	-0.08675	-0.02412
H	-1.54241	-1.37182	-0.29351
C	-2.81026	2.221559	0.419958
H	-0.74088	2.778466	0.556555
C	-3.72637	1.191301	0.219829
H	-4.79599	1.355804	0.249976
H	-3.16685	3.227231	0.621429
N	-4.18113	-1.19075	-0.24426
O	-3.71944	-2.31181	-0.4542
O	-5.38147	-0.92432	-0.20273

Tabel S8: Cartesian coordinate of optimized structure of anti cyanoPBA monomer

Atoms			
C	0.516368	0.383137	0.086348
C	1.03442	-0.81533	0.608641
C	2.398028	-1.07879	0.56795
C	3.280967	-0.1492	0.003216
C	2.777315	1.048432	-0.52143
C	1.411311	1.308029	-0.47875
H	0.364663	-1.53375	1.071933
H	2.801287	-1.99915	0.977117
H	3.455307	1.766732	-0.96862
H	1.030321	2.227007	-0.91456
C	4.729649	-0.48054	-0.01398
O	5.213823	-1.5034	0.427363
O	5.489564	0.490381	-0.58362
H	6.40786	0.165492	-0.53945
C	-0.94085	0.664472	0.129558
C	-1.4241	1.962947	0.373015
C	-1.87311	-0.36302	-0.07263
C	-2.79232	2.231312	0.412027
H	-0.7178	2.766777	0.557838
C	-3.23293	-0.07338	-0.02877
H	-1.55875	-1.37696	-0.28611
C	-3.71822	1.210296	0.209684
H	-3.13941	3.24099	0.609669
H	-4.78625	1.386121	0.234249
N	-4.19605	-1.1676	-0.25131
O	-5.39365	-0.8881	-0.21679
O	-3.74525	-2.29392	-0.45597

Table S9: Cartesian coordinate of optimized structure of nitroPBA dimer

Atoms			
C	6.220311	0.453656	-0.27972
C	5.397274	1.59366	-0.25422
C	4.013195	1.473125	-0.23398
C	3.414812	0.206413	-0.23742
C	4.224016	-0.93755	-0.25932
C	5.60889	-0.81216	-0.28081
H	5.847594	2.581397	-0.22241
H	3.378269	2.352226	-0.20673
H	3.762942	-1.91878	-0.2687
H	6.224137	-1.70596	-0.32477
C	1.931791	0.113804	-0.22014
O	1.21563	1.119517	-0.20781
O	1.463376	-1.124	-0.22113
H	0.458962	-1.11041	-0.21252
H	-5.8476	-2.5814	-0.22238
C	-5.39727	-1.59366	-0.25419
C	-6.22031	-0.45366	-0.2797
C	-4.0132	-1.47313	-0.23394
C	-5.60889	0.812156	-0.28079
C	-3.41481	-0.20642	-0.23738
H	-3.37827	-2.35223	-0.20668
C	-4.22401	0.937546	-0.25928
H	-6.22413	1.705958	-0.32475
C	-1.93179	-0.11381	-0.22009
H	-3.76294	1.918773	-0.26867
O	-1.21563	-1.11953	-0.2078
O	-1.46337	1.123986	-0.22102
H	-0.45896	1.110394	-0.21251
C	-7.69901	-0.58473	-0.30674
C	-8.51079	0.317909	0.394683
C	-8.32324	-1.61411	-1.03458
C	-9.89347	0.171817	0.352732
H	-8.08505	1.115899	0.99003
C	-9.71177	-1.74275	-1.06208

H	-7.71247	-2.30722	-1.60524
C	-10.5179	-0.84634	-0.36403
H	-11.5981	-0.9189	-0.3661
C	7.699014	0.584727	-0.30676
C	8.510786	-0.31791	0.394681
C	8.323246	1.614104	-1.03459
C	9.893472	-0.17181	0.352741
H	8.085043	-1.1159	0.990028
C	9.711779	1.742754	-1.06208
H	7.712476	2.307216	-1.60526
C	10.51791	0.84634	-0.36402
H	11.59815	0.918909	-0.36608
N	-10.7281	1.128459	1.102952
O	-11.9479	0.974415	1.061813
O	-10.1557	2.023906	1.722858
H	-10.169	-2.54165	-1.63797
N	10.7281	-1.12845	1.10297
O	11.94793	-0.97439	1.061854
O	10.15567	-2.02388	1.722891
H	10.16899	2.541651	-1.63797

Table S10: Geometric parameters of nitroPBA monomer and dimer optimized at the DFT/B3LYP/6-31G* level

	monomer	dimer
	Bond lengths / Å	
C–C (Phenyl) ¹	1.3968	1.3967
C–C (Benzoic acid) ²	1.3991	1.3991
O–H (calboxyl)	0.9751	1.0045
O–H (carboxyl)	–	1.6746
	Angle / degree	
benzene-benzene ³	37.4	37.0
benzene-nitro ⁴	0.4	0.7

¹ Averaged C–C bond length of benzene ring in phenyl group

² Averaged C–C bond length of benzene ring in benzoic acid

³ The distortion angle between benzene rings

⁴ The distortion angle between benzene ring (in phenyl group) and nitro group

Table S11: Frequencies calculated at the DFT/B3LYP/6-31G* level for nitroPBA dimer

Frequencies / cm ⁻¹					
4.5519	314.479	698.3932	985.9969	1315.505	1639.187
13.8841	324.9055	698.7321	986.0181	1315.551	1639.341
18.8501	376.015	712.3003	995.4345	1327.659	1667.891
26.0622	376.1109	714.1193	995.538	1330.224	1668.187
42.6843	417.8078	748.3632	997.9527	1343.083	1679.935
44.0493	419.5104	748.4001	997.9642	1343.436	1679.954
45.6538	419.8153	762.2127	1018.624	1360.24	1721.307
52.9844	420.2778	769.7392	1018.644	1361.224	1765.639
54.976	442.5679	784.6167	1035.236	1365.918	3088.975
68.8851	442.9738	784.8353	1035.713	1365.924	3184.253
75.4951	457.8395	823.1966	1066.869	1399.273	3199.599
77.6789	475.5246	827.572	1066.939	1399.456	3199.733
82.1458	495.5085	828.2997	1121.061	1446.135	3203.542
89.2502	503.4748	830.9555	1121.067	1446.149	3203.722
97.5216	529.0821	863.7846	1127.135	1472.864	3204.334
117.9172	548.8119	863.8521	1127.231	1480.681	3204.396
148.9486	558.1884	876.4496	1147.51	1482.734	3217.244
158.5717	563.1238	876.894	1147.525	1510.686	3217.256
181.8978	572.7255	893.3167	1159.619	1525.632	3230.862
182.2614	574.2266	893.3271	1163.015	1525.803	3230.867
223.2107	647.753	916.6032	1204.294	1562.446	3237.333
227.5979	648.3645	939.3249	1204.302	1562.763	3237.36
245.4244	655.2567	939.327	1221.217	1611.591	3252.831
259.2905	657.5833	958.5517	1222.534	1612.581	3252.832
278.0449	690.8047	958.554	1301.85	1627.373	3256.553
278.2401	696.036	964.504	1301.866	1627.504	3256.553

4. Scaling factor for both cyanoPBA and nitroPBA

Figure S2: Plots of the experimental wavenumber (y) for ACBC-16 (top) and ANBC-16 (bottom) versus the calculated wavenumber (x) at the B3LYP/6-31G* level. Correlation factors (r) are also shown. With the scaling equation $y=a_0+a_1x$, the scaling factor (a_1) was determined and the average of the values was used as a common scaling factor for both cyanoPBA and nitroPBA.