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Supporting Information on

"New Type of Organic-Inorganic Hybrid NLO-Phores with Large Off-Diagonal First Hyperpolarizability Tensors: A Two-Dimensional Approach"

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Table S1. Computed static first hyperpolarizability values ($\times 10^3$ a.u.) for systems **1**, **2**, **3**, and **4** at different levels of theory

Chem. Model No.	Methods	β_{zzz}	β_{zyy}	β_z
1	**B3LYP**	0.04	0.04	0.08
	PBE0	0.04	0.04	0.08
	mPW1PW1	0.04	0.04	0.08
	B3P86	0.04	0.04	0.08
	B3PW91	0.05	0.03	0.08
	O3LYP	0.04	0.04	0.08
2	**B3LYP**	0.13	0.32	0.45
	PBE0	0.13	0.32	0.45
	mPW1PW1	0.12	0.29	0.41
	B3P86	0.13	0.32	0.45
	B3PW91	0.13	0.32	0.45
	O3LYP	0.13	0.36	0.49
3	**B3LYP**	2.03	11.94	13.97

	PBE0	1.92	10.95	12.87
	mPW1PW1	1.88	10.72	12.6
	B3P86	2.04	11.98	14.02
	B3PW91	2.05	12.03	14.08
	O3LYP	2.32	14.58	16.9
4	**B3LYP**	7.10	42.51	49.61
	PBE0	6.35	36.65	43
	mPW1PW1	6.24	35.76	42
	B3P86	7.15	42.82	49.97
	B3PW91	7.15	42.93	50.08
	O3LYP	9.07	59.67	68.74

Table S2. All the ten first hyperpolarizability tensor components ($\times 10^3$ a.u.) of all the studied systems as produced by Polar = Enonly[a] keyword by GAUSSIAN calculations

	β_X			β_Y				$\boldsymbol{\beta_Z}$	
	β_{xxx}	β_{xyy}	β_{xzz}	β_{yyy}	β_{yzz}	β_{xxy}	β_{xxz}	$\boldsymbol{\beta_{zzz}}$	$\boldsymbol{\beta_{zyy}}$
Sys.					Set-I				
1	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.04
2	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.13	0.31
3	0.00	0.00	0.02	0.00	0.00	0.00	0.09	2.03	11.94
4	0.00	0.00	0.07	0.06	0.00	0.00	0.15	7.09	42.51
					Set-II				
3A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.85	-27.12
3N	0.00	0.00	0.01	0.01	0.00	0.00	-0.34	-1.15	-33.01
4A	0.00	0.00	0.03	-0.06	0.00	0.00	-0.06	-1.92	-60.37
4N	0.00	0.00	-0.04	-20.14[b]	-14.03[b]	0.00	-0.47	-15.77	-261.14

[a] Sign conventions for tensor components of β_z are reversed according to the signs of $\Delta\mu$, which are the only factors in two-level expression to determine the sign of tensor components. [b] The nonzero components of system **4N** are neglected because our major focus in present investigation is on diagonal (β_{zzz}) and off-diagonal (β_{xyy}) components of first hyperpolarizability (β_Z) along the z-axis.

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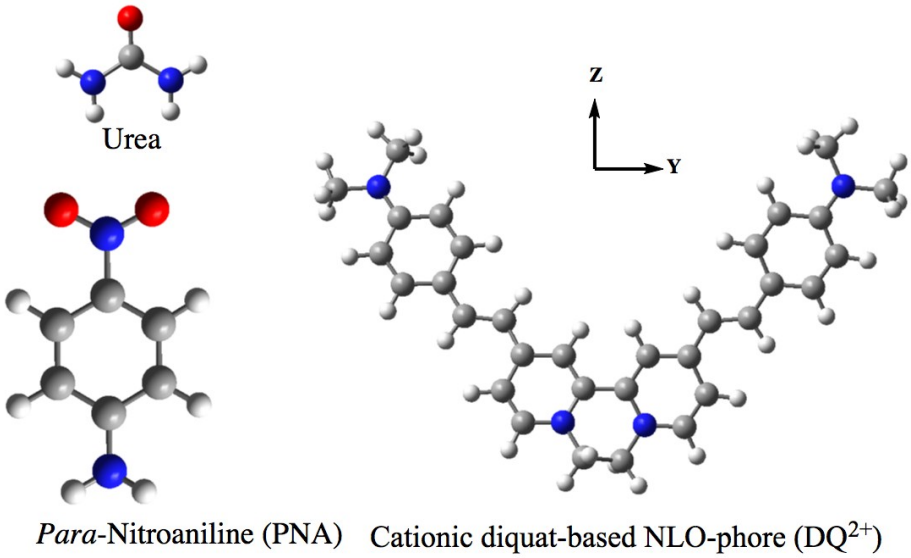

Figure S1. Structures of reference systems at B3LYP/6-311G* level of theory

Table S3. Off-diagonal (β_{zyy}) and diagonal (β_{zzz}) components of β_z calculated by the two-level expression (Eq. 3) with full set of their parameters (all units are in a. u.)

Off-diagonal (β_{zyy})					
Systems	**Transitions**	$\Delta\mu_z$	ΔE	μ_y^0	β_{zyy}
1	$S_0 \rightarrow S_3$	0.79	0.1879	0.342	16
2	$S_0 \rightarrow S_1$	0.77	0.1554	1.413	382
3	$S_0 \rightarrow S_1$	2.49	0.1020	3.463	17215
4	$S_0 \rightarrow S_1$	5.06	0.0876	4.357	75085
3A	$S_0 \rightarrow S_1$	-0.5	0.0578	5.047	-22868
3N	$S_0 \rightarrow S_1$	-0.33	0.0501	6.585	-34270
4A	$S_0 \rightarrow S_1$	-0.48	0.0480	8.015	-80439
4N	$S_0 \rightarrow S_1$	-1.4	0.0520	8.719	-235817
Diagonal (β_{zzz})					
Systems	**Transition**	$\Delta\mu_z$	ΔE	μ_z^0	β_{zzz}
1	$S_0 \rightarrow S_1$	0.79	0.1747	0.671	70
2	$S_0 \rightarrow S_2$	0.77	0.1503	0.35	25
3	$S_0 \rightarrow S_2$	2.49	0.1115	1.331	2129
4	$S_0 \rightarrow S_2$	5.06	0.0923	1.586	8968
3A	$S_0 \rightarrow S_2$	-0.5	0.0667	1.283	-1110
3N	$S_0 \rightarrow S_2$	-0.33	0.0647	2.01	-1910
4A	$S_0 \rightarrow S_2$	-0.48	0.0630	2.103	-3214
4N	$S_0 \rightarrow S_2$	-1.4	0.0520	2.27	-15984