Supporting Information

Exploring the Possible Existence of Oxygen-bridged Planarized 4-aminopyridine: Promising Structure, Charge transport and Nonlinear Optical Properties

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Table S1. The maximum absorption wavelengths/energies along with other important transition parameters for APY_3 different levels of theory

Transition Parameters	**APY_3** B3LYP	**APY_3** PBE0	**APY_3** M06	**APY_3** **Exp.** [a]
λ_{max} (nm)	301.0	292.5	293.8	**302.0**
λ_{max} (eV)	4.121	4.238	4.219	**4.11**
f_0	0.277	0.288	0.270	**--**
Transition	H->L	H->L	H->L	**--**
% C. I.	70	70	69	**--**
E_{LUMO}	-1.423	-1.296	-1.331	**-2.09**

[a] All experimental (Exp.) values have taken from reference[1]

Table S2. The average third-order nonlinear polarizabilities (<γ>, $\times 10^{-36}$ esu) along with their individual components for APY_3, APY_3O_3 different methods at 6-311G** basis set.

	APY_3				**APY_3O_3**			
γ	B3LYP	PBE0	M06	MP2	B3LYP	PBE0	M06	MP2
γ_{xxxx}	6.147	8.625	8.633	0.8802	0.924	0.9212	0.4187	0.8502
γ_{yyyy}	135.38	116.33	112.19	43.568	163.15	149.68	147.96	45.326
γ_{zzzz}	135.08	110.00	10.544	43.272	163.23	149.59	147.24	45.318
γ_{xxyy}	4.443	10.275	10.079	2.9172	2.9360	49.898	49.298	1.5982
γ_{xxzz}	4.549	11.988	11.862	2.9723	2.3987	2.1097	2.0207	1.4201
γ_{yyzz}	44.846	37.522	35.944	1.4453	53.901	2.0480	1.8175	1.4966
<γ>	76.856	70.908	68.392	26.407	89.16	81.661	80.387	25.507

The results presented in Table S2 shows that MP2 has lower amplitudes than the DFT methods. Basically both approaches are different i.e. DFT methods variational and parameterized that are based on electron density and while MP2 is perturbation-based method like ab initio. Firstly, it is important to mention that MP2 is usually considered as better method due to electron correlation but several reports showed the hybrid approach and empirical parameterizations sometimes give advantage to DFT methods while comparing their results with experiments.[2-4] For instance, Yu et al., [5] have performed several benchmark calculations for para-nitroaniline (PNA), 4-hydroxy-4 -nitrostilbene (HONS) and 4-hydroxy-4 -nitrobenzene (HONB) etc. and compared the values with experimental results. They concluded that even MP2 results agreement does not appear to be perfect because the best agreement with experiment is found for the HONS / p-NA molecular pair with 8% underestimation while the worst is for the HONS/HONB molecular pair with 72% overestimation. Secondly, the applicability of MP2 is limited with relatively small systems due to its extensive computational costs (N^5). In short, we do think the DFT results agree with each other and these make a qualitative understanding irrespective of other methodologies.

Table S3. The individual components of γ for $TPBO_3$, APY_3O_3, APY_3O_3 - $TPBO_3$ dimer and $\gamma_{induced}$ (**APY_3O_3 − $TPBO_3$**)-(**APY_3O_3 + $TPBO_3$**) at B3LYP/6-311G** level of theory

	$TPBO_3$	**APY_3O_3**	**APY_3O_3 - $TPBO_3$ dimer** [a]	**$\gamma_{induced}$**
γ	$\times 10^{-36}$ esu	$\times 10^{-36}$ esu	$\times 10^{-36}$ esu	$\times 10^{-36}$ esu
γ_{xxxx}	1.947	0.924	130.00	127.119
γ_{yyyy}	146.11	163.15	237.41	-71.85
γ_{zzzz}	146.30	163.23	237.82	-71.71
γ_{xxyy}	3.1952	2.9360	20.944	14.8128
γ_{xxzz}	3.1157	2.3987	21.419	15.9046
γ_{yyzz}	48.7385	53.901	78.748	-23.8915
<γ>	80.891	89.16	169.38	-0.671

References

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