Electronic supplementary information (ESI)

Towards an understanding of structure-nonlinearity relationships in triarylamine-based push-pull electro-optic chromophores: the influence of substitutent and molecular conformation on molecular hyperpolarizabilities

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1. Comparison of the trends in hyperpolarizability predicted by our calculations with experimental data.

For EO chromophores with different electron acceptors **4**, **5**, and **6**, our calculations show hyperpolarizabilities increase in the order of 4 ($\beta_{1907} = 147 \times 10^{-30} \text{ esu}$) < **5** ($\beta_{1907} = 178 \times 10^{-30} \text{ esu}$) < **6** ($\beta_{1907} = 280 \times 10^{-30} \text{ esu}$). The hyperpolarizability β values of these three chromophores were measured experimentally at 802 nm in CHCl₃. Chromophore **4** has the lowest β value ($\beta_{802} = 1000 \times 10^{-30} \text{ esu}$), then chromophore **5** ($\beta_{802} = 5000 \times 10^{-30} \text{ esu}$), and chromophore **6** has the highest β value ($\beta_{802} = 20,000 \times 10^{-30} \text{ esu}$); the order from experimental data is **4** < **5** < **6**.¹

For EO chromophores with different numbers of methoxy groups on *para* positions of the TAA moiety **7**, **8**, and **9**, our calculations show hyperpolarizabilities increase in the order of **7** (β_{1907} = 321 x 10⁻³⁰ esu) < **8** (β_{1907} = 342 x 10⁻³⁰ esu) < **9** (β_{1907} = 358 x 10⁻³⁰ esu). The hyperpolarizability β values of these three chromophores were measured experimentally at 1907 nm in CHCl₃. Chromophore **7** has the lowest β value (β_{1907} = 1770 ± 89 x 10⁻³⁰ esu), then chromophore **8** (β_{1907} = 2150 ± 259 x 10⁻³⁰ esu), and chromophore **9** has the highest β value (β_{802} = 3456 ± 128 x 10⁻³⁰ esu); the order from experimental data is **7** < **8** < **9**.²

The trends in hyperpolarizability predicted from our calculations match the trends from experimental data.

2. Methoxy group substituted NLO chromophores

2.1. Polarizability ($\alpha_{average}$), second-order polarizability (β), energy and dipole moment (μ).

ESI-Table 1 lists the average polarizability ($\alpha_{average}$), second-order polarizability (β), energy, and dipole moment (μ) of the model NLO chromophores and natural triarylamine molecule.

We found the NLO chromophores with the same number of methoxy groups on the TAA moiety have similar $\alpha_{average}$ values no matter where the methoxy group is located. For example, mono-methoxy substituted NLO chromophores, 10-14, have similar $\alpha_{average}$ values around 420

a.u. and the $\alpha_{average}$ values of di-methoxy substituted NLO chromophores are around 444 a.u. Introduction of more methoxy group on the TAA moiety enhances the $\alpha_{average}$ values.

A detailed discussion of second-order polarizability (β) is found in the main paper. Briefly, introduction of several methoxy groups on appropriate locations of the TAA moiety can dramatically increase the second-order polarizability of the NLO chromophore.

Stronger electron acceptor groups have lower total energy when they have the same electron donor and bridge (cf. 4 > 5 > 6 > 9). Introducing more methoxy groups on the TAA moiety causes the total energy to decrease (cf. 8 > 9; $1 \sim 3 > 10 \sim 14 > 4$, $15 \sim 18 > 19$, 20 > 21 > 22). NLO chromophores with the same number of methoxy group on the TAA moiety have similar total energy no matter where the methoxy groups are located. The difference in the HOMO and LUMO energies of all models is very small. Model chromophore 22 has the highest HOMO and LUMO energy of all model chromophores. Chromophores with the strongest electron acceptor (CF₃-Ph-TCF) have the lowest LUMO energy. And model 13 with di-*ortho* substituted methoxy groups on the phenyl ring connected with the bridge and electron acceptor group has the lowest HOMO energy. Chromophores with four methoxy groups on the *ortho* positions of ring B and ring C (19, 21 and 22) have higher HOMO energies, which may be due to steric effects.

The average dipole moments (μ) are from 0.019 Debye (natural TAA) to 13.59 Debye (**model** 9). Model chromophores with stronger electron acceptors have larger dipole moment μ values (cf. 4 < 6 < 9). Introduction of a methoxy group on the *ortho* positions of ring B and ring C can effectively increase the dipole moment. Model chromophore 22 with the largest number of methoxy groups on the TAA moiety has the largest dipole moment of models with the same bridge and electron acceptor.

2.2. C-N bond lengths and torsion angles

The bond lengths between the central nitrogen atom and the carbon atoms of the three phenyl rings are listed in table 2. The Ph-N bond lengths are indicative of the delocalization of the nitrogen lone pair into the aryl ring. Except for model **13** and model **17**, the bond length (C-N ring A) between the central nitrogen and the phenyl ring which connects with the bridge and electron acceptor is shorter than the bond lengths (C-N ring B and C-N ring C) between the central nitrogen and the other two phenyl rings. The difference in model **13** and model **17** is that phenyl ring A rotates out of the central NCCC reference plane because of steric effects, and the nitrogen lone pair predominately delocalizing into the other two phenyl rings. Model chromophores with different electron acceptors (**4**, **5**, **6**, **7-9**) have similar values in the C-N ring A bond length. The C-N ring A bond lengths of model chromophore **15** and **20** are the shortest of all studied model chromophores, which also have the smallest torsion angle \angle A (around 3°) and the largest torsion angles \angle B and \angle C. In model chromophores **15** and **20**, the nitrogen lone pair predominately delocalizes into ring A due to the molecular conformational effect.

The three torsion angles between the central NCCC reference plane and the three phenyl rings, respectively, are listed in ESI-table 2. The torsion angles are important parameters to quantitatively measure the molecular conformations of the TAA moiety and help us to

understand the delocalization of the nitrogen lone pair into the three phenyl rings. The natural triarylamine molecule is symmetrical and has torsion angles of about 35°. Introduction of methoxy groups on the *para* positions of ring B and ring C causes sight changes in all three torsion angles. Introduction of methoxy groups on the *ortho* positions of ring B and ring C causes dramatic changes in all three torsion angles. All these changes lead to larger delocalization of the nitrogen lone pair into ring A which connects with the thiophene bridge and electron acceptor and less delocalization of the central nitrogen lone pair into the other two rings.

model	$\alpha_{average}$	β ₁₉₀₇	номо	LUMO	Total Energy	μ
	(au)	(10 ⁻³⁰ esu)	(EV)	(EV)	(EV)	(Debye)
1	398	105	-7.989	-1.665	-4656.80026	5.317
2	403	114	-8.002	-1.641	-4656.80439	5.949
3	406	121	-8.041	-1.638	-4656.76928	6.889
4	449	147	-7.933	-1.587	-5608.46515	8.142
5	545	178	-7.921	-1.7	-7222.3705	7.497
6	589	280	-7.962	-2.091	-7254.57921	11.164
7	607	321	-8.061	-2.323	-8384.17799	11.381
8	630	342	-7.977	-2.321	-8860.04062	12.324
9	649	358	-7.974	-2.289	-9335.8765	13.59
10	427	131	-7.963	-1.621	-5132.61544	6.629
11	420	131	-8.065	-1.531	-5132.50926	8.392
12	421	104	-8.082	-1.643	-5132.62793	5.529
13	415	69	-8.229	-1.679	-5132.43179	5.701
14	426	127	-8.031	-1.52	-5132.599	8.534
15	441	172	-7.916	-1.453	-5608.25595	9.918
16	444	159	-7.875	-1.491	-5608.16847	9.827
17	432	43	-7.988	-1.788	-5608.1577	2.624
18	444	111	-8.082	-1.652	-5608.47797	6.616
19	481	183	-7.682	-1.4	-6559.57179	12.368
20	482	185	-7.894	-1.443	-6560.01286	10.343
21	522	199	-7.613	-1.381	-7511.30433	12.482
22	543	216	-7.58	-1.281	-7987.14361	13.288
TAA	225	0.05	-7.956	0.179	-2715.96049	0.019
23	449	146	-7.78	-1.581	-5188.41714	8.727
24	441	131	-7.977	-1.556	-5188.29214	8.105
25	438	99	-8.029	-1.558	-5188.33941	7.379
26	491	174	-7.673	-1.515	-5720.06225	10.603
27	478	161	-7.984	-1.501	-5719.70182	8.483
28	562	221	-7.742	-1.439	-6783.08678	10.679
29	632	216	-7.334	-1.399	-7845.69969	10.398
30	523	188	-7.904	-1.452	-6671.57933	11.11
31	566	242	-7.397	-1.308	-7622.85714	15.45
32	586	247	-7.408	-1.203	-8098.70935	17.11

ESI-Table 1. The polarizabilities (a.u.), second-order polarizabilities (10^{-30} esu), energy and dipole moment (μ) of designed NLO chromophores and the natural triphenylamine molecule.

model	C-N bond	C-N bond	C-N bond	∠ A	∠ B	∠ C
	(Å) Ra	(Å) Rb	(Å) Rc	Ring A	Ring B	Ring C
1	1.409	1.414	1.416	31.58	35.68	37.15
2	1.408	1.416	1.417	29.94	36.32	37.9
3	1.408	1.415	1.417	30.68	35.56	37.87
4	1.406	1.421	1.421	21.73	45.77	47.46
5	1.405	1.419	1.42	24.45	44.71	43.91
6	1.407	1.421	1.42	24.06	45.29	44.62
7	1.408	1.415	1.416	30.55	36.16	37.41
8	1.406	1.418	1.415	28.05	41.77	37.18
9	1.407	1.422	1.421	22.82	45.88	47.23
10	1.406	1.418	1.415	27.06	42.52	37.83
11	1.408	1.426	1.423	17.89	79.02	48.08
12	1.409	1.414	1.416	31.92	34.94	37.57
13	1.421	1.422	1.422	51.41	35.42	35.22
14	1.407	1.416	1.416	28.75	38.27	38.45
15	1.396	1.422	1.423	2.58	84.95	89.54
16	1.403	1.421	1.423	16	54.78	62.04
17	1.418	1.414	1.409	85.79	36.17	29.26
18	1.41	1.414	1.415	33.15	34.77	35.51
19	1.404	1.419	1.417	15.9	62.04	56.45
20	1.397	1.423	1.424	2.81	84.6	86.12
21	1.404	1.418	1.42	15.03	56.56	64.96
22	1.401	1.417	1.418	16.78	57.56	64.86
TAA	1.413	1.413	1.413	34.31	34.36	35.15
23	1.406	1.419	1.414	26.94	42.72	37.55
24	1.407	1.423	1.414	27.32	60.25	34.73
25	1.41	1.415	1.415	30.81	37.14	36.79
26	1.406	1.423	1.423	19.55	49.42	49.68
27	1.405	1.418	1.418	7.45	62.53	75.59
28	1.39	1.423	1.423	4.2	75.05	77.37
29	1.407	1.417	1.417	35.3	49.32	49.48
30	1.402	1.427	1.426	4.75	86.58	80.03
31	1.402	1.418	1.42	13.36	56.74	66.58
32	1.401	1.419	1.42	12.55	57.24	67.04

ESI-Table 2: The bond lengths between the central nitrogen and the carbon atom of the three phenyl rings of the TAA donor moiety and the torsion angles between the central NCCC plane and the three phenyl rings of the TAA moiety.



ESI-Scheme one: the structures of chromophore 4 and 10-22.

3. Dimethylamino substituted TAA based chromophores 23-29

Based on our discoveries on methoxy substituted chromophores, a series of dimethylamino substituted TAA based chromophores were designed and studied. Three important positions on the three phenyl rings were studied: the *para* and *ortho* positions on ring B and ring C and the *meta* position on ring A. Chromophores with different numbers (1, 2, 4, and 6) of dimethylamino groups on the three phenyl rings were investigated.

Because the dimethylamino group is a stronger electron donor group than the methoxy group, mono- and di-*para*-dimethylamino substituted chromophores display higher β_{1907} values than that of methoxy substituted analogues. [cf. **23** ($\beta_{1907} = 146 \times 10^{-30}$ esu) vs. **10** ($\beta_{1907} = 131 \times 10^{-30}$ esu) and **4** ($\beta_{1907} = 147 \times 10^{-30}$ esu) vs. **26** ($\beta_{1907} = 174 \times 10^{-30}$ esu)].

Introduction of dimethylamino groups on the *ortho* position(s) of the TAA moiety also can cause molecular conformational changes due to steric effects. However, the conformational effect is less than that of the methoxy group, because the torsion angles between ring B or ring C and the central CCCN plane are smaller than their methoxy group substituted counterparts. [cf. 11 ($\angle B = 79^\circ$) vs 24 ($\angle B = 63^\circ$), 15 ($\angle B = 85^\circ$ and $\angle C = 90^\circ$) vs 27 ($\angle B = 63^\circ$ and $\angle C = 76^\circ$), and 20 ($\angle B = 85^\circ$ and $\angle C = 86^\circ$) vs. 28 ($\angle B = 75^\circ$ and $\angle C = 77^\circ$)].

Introduction of a dimethylamino group on the *meta* position of ring A yields a large decrease in hyperpolarizability (cf. **25** vs **3**). This may be because the steric effect of the larger dimethylamino group compromises the planarity of the conjugated system of phenyl ring A, bridge, and electron acceptor, resulting in the decrease in hyperpolarizability.

Fig **SI-1** shows isosurfaces of the HOMO for di-substituted chromophore **27**. There are small contributions from the lone pair electrons on the nitrogen atoms in *ortho*-substituted dimethylamino groups on phenyl ring B and ring C. Both the electron donor effect and molecular conformational effect contribute to the increase in hyperpolarizability compared to nonsubstituted TAA chromophore **3**.

Introducing more dimethylamino groups onto the TAA moiety yield a large increase in hyperpolarizability (cf. **26** vs **28**). Chromophore **28**, with two dimethylamino groups on *ortho* positions and two methoxy groups on *para* positions of ring B and C of the TAA donor moiety, respectively, has the largest β_{1907} value ($\beta_{1907} = 221 \times 10^{-30}$ esu). As we discussed in the main paper, both an electronic donor effect and molecular conformational effect contribute to this increase in hyperpolarizability. Fig **SI-1** also plots isosurfaces of the HOMO for di-substituted chromophore **28**. There are small contributions from the lone pair electrons on the nitrogen atoms in *ortho*-substituted dimethylamino groups on phenyl ring B and ring C.

Dimethylamino substituted chromophore **28** has a larger β_{1907} value than its methoxy substituted counterpart, chromophore **22** (cf. **28**, $\beta_{1907} = 221 \times 10^{-30}$ esu vs. **22**, $\beta_{1907} = 216 \times 10^{-30}$ esu), however, chromophore **22** has a much larger dipole moment than chromophore **28** (cf. **22**, $\mu = 13.3$ D vs **28**, $\mu = 10.7$ D). Introduction of methoxy groups on the *ortho* position of the TAA moiety has larger effect on the molecular dipole moment than that of dimethylamino groups.

Overall, introduction of dimethylamino groups on both *para* and *ortho* positions of ring B and ring C of the TAA moiety can effectively improve the hyperpolarizability (cf. **28** and **29**). *Ortho*

substitution can affect the molecular conformations of the TAA moiety by a steric effect. However, this effect is less than their methoxy substituted counterparts. *Ortho* dimethylamino substitution has less effect on the dipole moment than *ortho* methoxy substitution. Introduction of a dimethylamino group on the *meta* position of ring A causes a large decrease in hyperpolarizability.



ESI-Scheme two: the structures of dimethylamino substituted TAA based chromophores.



Figure S-1. The frontier molecular orbitals (HOMO and LUMO) of model NLO chromophores **27** and **28** (left); and isosurfaces of the HOMO for phenyl ring B or phenyl ring C in the TAA moiety of model NLO chromophores **27** and **28** (right).

4. The hybrid substituted TAA based chromophores

Because the dimethylamino group is a better electron donor than the methoxy group, and because the methoxy group is a better group to control the molecular conformation than the dimethylamino group, we designed several hybrid substituted model chromophores with two dimethylamino groups on the *para* positions of ring B and ring C and different numbers of methoxy groups on other important positions.

Further increases in both hyperpolarizability and dipole moment were achieved by replacing methoxy groups with dimethylamino groups on the *para* positions of chromophore **22** (cf. **22**, $\beta_{1907} = 216 \times 10^{-30}$ esu vs **32**, $\beta_{1907} = 247 \times 10^{-30}$ esu) and (cf. **22**, $\mu = 13.3$ D vs **32**, $\mu = 17.1$ D). Chromophore **32** with two dimethylamino groups on the *para* positions of ring B and ring C, four methoxy groups on the *ortho* positions of ring B and ring C, and one methoxy group on the *meta* position of ring A gives the highest hyperpolarizability and dipolar moment of all designed model molecules. The β_{1907} value of chromophore **32** is 104% higher than its nonsubstituted analogue **3** (cf. **3**, $\beta_{1907} = 121 \times 10^{-30}$ esu vs **32**, $\beta_{1907} = 247 \times 10^{-30}$ esu).



ESI-Scheme three: the structures of hybrid substituted TAA based chromophores.

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- 2. Y. J. Cheng, J. D. Luo, S. Hau, D. H. Bale, T. D. Kim, Z. W. Shi, D. B. Lao, N. M. Tucker, Y. Q. Tian, L. R. Dalton, P. J. Reid and A. K. Y. Jen, *Chem Mater*, 2007, 19, 1154-1163.