Electronic supplementary information (ESI)

Efficient π Bridges Base on Five-membered Heterocyclic for Second-order NLO Property of the Push-pull Type Molecules

Yan Ji *, Ying Qian, Wei Lu
School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189; China

1 Dipole moment (μ) and energy

The table 1 list the dipole moment and energy of the molecules M1~M16 and MZ-1~MZ16. The dipole moments (μ) are from 5.231 Debye (M-12) to 17.663 Debye (M-5). When compared the N,N-dimethylaniline group (Rd1) and triphenylamine group (Rd2), the μ of molecules (M-1~M-8 and MZ-1~MZ-8) are larger than the μ of molecules (M-9~M16 and MZ-9~MZ-16). These can show the giving electronic capability of Rd1 is larger than that of Rd2. To compare with the 2-(3-cyano-4,5,5-trimethylfuran-2-ylidene)malononitrile group (TCF Ra2) and benzonitrile group (Ra1), the μ of molecules (M-1~M-4, M-9~M-12; MZ-1~MZ-4, MZ-9~MZ-12) are smaller than the μ of molecules (M-5~M-8, M-13~M-16; MZ-5~MZ-8, MZ-13~MZ-16) that show the Ra2 is a high pulling electronic group. These due to the TCF group is a stronger electronic accepter than benzonitrile group.

When considered the five-membered heterocyclic p-π conjugated bridge, the X atoms are O, S, NH, and PH respectively. The μ of heterocyclic contribution did not have the regular rules with the changing of the X atoms.

ESI-Table1. the dipole moment(μ) and energy of designed molecules.

	μ (Debye)	TOTAL E (EV)	HOMO (EV)	LUMO (EV)		μ (Debye)	TOTAL E (EV)	HOMO (EV)	LUMO (EV)
M-1	7.272	-3463.831	-8.025	-1.129	MZ-1	8.768	-3550.262	-8.492	-1.345
M-2	7.965	-3347.280	-8.179	-1.016	MZ-2	9.046	-3433.464	-8.432	-1.508
M-3	8.086	-3366.089	-8.091	-0.857	MZ-3	10.164	-3452.313	-8.507	-0.876
M-4	6.946	-3329.119	-8.130	-0.822	MZ-4	9.287	-3415.358	-8.317	-1.379
M-5	17.663	-4507.219	-8.438	-2.269	MZ-5	10.777	-4593.541	-8.691	-2.594
M-6	17.255	-4390.654	-8.484	-2.265	MZ-6	14.076	-4476.773	-8.643	-2.558
M-7	13.986	-4409.512	-8.435	-2.161	MZ-7	12.288	-4495.624	-8.642	-2.482
M-8	16.081	-4372.473	-8.356	-2.198	MZ-8	14.809	-4458.687	-8.592	-2.457
M-9	5.650	-4741.509	-8.066	-1.075	MZ-9	7.441	-4827.904	-8.396	-1.434
M-10	5.718	-4624.958	-8.110	-1.163	MZ-10	7.614	-4711.109	-8.326	-1.624
M-11	5.705	-4643.759	-8.057	-0.912	MZ-11	9.022	-4729.961	-8.367	-0.905
M-12	5.231	-4606.809	-8.051	-0.889	MZ-12	6.867	-4693.018	-8.231	-1.535
M-13	12.726	-5784.844	-8.272	-2.330	MZ-13	10.002	-5871.167	-8.582	-2.642
M-14	15.359	-5668.310	-8.371	-2.344	MZ-14	16.952	-5754.360	-8.544	-2.578
M-15	13.541	-5687.167	-8.334	-2.226	MZ-15	11.153	-5773.258	-8.497	-2.535
M-16	13.733	-5650.164	-8.274	-2.270	MZ-16	13.548	-5736.321	-8.482	-2.514

The total energy decreased along about the order number of molecules from 1 to 16 except some molecules (M-5, M-13, MZ-5, and MZ-13). Compared the contribution of groups for energy decreasing are Rd2>Rd1; Ra2>Ra1; X1>X3>X2>X4. As shown from the order, the O atom can decrease the energy of molecules to make the molecules more stable. Compared the HOMO and LUMO energy, the Ra2 can decrease the energy of molecules more than that of Ra1. The contribution of Rd1 and Rd2 to the HOMO and LUMO energy is seemly same. The energy of M groups are larger than that of MZ groups that show the heterocyclic bridge with three heteroatom is more stable than one heteroatom bridge. The lowest energy molecule is MZ-13, which due to the Rd2 has N atom and three-phenyl cyclic to forming the large p-π conjugated system.

2 Polarizability

The polarizabilities (α) of molecules (M-1~M-16 and MZ-1~MZ-16) are listed on the table 2. Compared the $\alpha_{average}$, the α values of molecules (M-9~M-16) are larger than that of molecules (M-1~M-8); and the α of molecules (MZ-9~MZ-16) are larger than that of molecules (MZ-1~MZ-8). These can show the group Rd2 increase the α values of molecules larger than group Rd1; and the group Ra2 can increase the α of molecules larger than group Ra1, which can show the large conjugated system can increase the α values of molecules.

Compared the different X atom of the heterocyclic bridge, the result show the α values of molecules (M-1~M-16) have the order of S≈PH>O≈NH; and the α of molecules (MZ-1~MZ-16) have the order of PH≈S>O≈NH. These shows the S atom and P atom can help to enhance the α values of molecules. From the table 2, the α of group M are larger than that of group MZ, which show the molecules with the one-heteroatom bridge have the larger α values than that of three-heteroatom bridge. The molecule M-14 gives the α_{max} (572.724a.u.).

ESI-Table 2. The polarizabilities (a.u.) of designed molecules.

	α_{xx}	α_{yy}	α_{zz}	$\alpha_{average}$		α_{xx}	α_{yy}	α_{zz}	$\alpha_{average}$
M-1	491.653	317.282	143.639	317.525	MZ-1	466.720	273.299	151.631	297.217
M-2	526.747	301.968	178.524	335.746	MZ-2	550.469	285.965	158.327	331.587
M-3	489.078	274.013	178.304	313.798	MZ-3	478.986	247.785	153.842	293.538
M-4	505.335	276.180	198.977	326.831	MZ-4	582.080	260.872	172.798	338.583
M-5	749.814	340.887	180.467	423.723	MZ-5	546.144	408.808	173.764	376.239
M-6	756.879	364.034	204.849	441.921	MZ-6	684.467	396.695	183.681	421.614
M-7	624.653	407.669	202.382	411.568	MZ-7	593.226	384.332	181.534	386.364
M-8	652.055	397.016	222.424	423.832	MZ-8	702.365	375.487	197.630	425.161
M-9	608.028	437.987	258.833	434.949	MZ-9	605.172	399.110	261.859	422.047
M-10	709.044	453.800	264.746	475.863	MZ-10	723.264	428.674	251.895	467.944
M-11	664.168	407.553	256.701	442.807	MZ-11	577.995	380.710	284.939	414.548
M-12	641.094	437.014	271.075	449.728	MZ-12	721.394	389.389	278.826	463.203
M-13	697.355	583.773	284.979	522.036	MZ-13	678.191	543.527	277.977	499.898
M-14	919.464	514.122	284.585	572.724	MZ-14	908.950	492.470	286.259	562.560
M-15	753.398	567.924	278.048	533.123	MZ-15	738.674	517.994	288.063	514.910
M-16	823.706	461.910	360.116	548.577	MZ-16	844.272	506.186	304.295	551.584

3 Second-order Polarizability

ESI-Table 3. The second-order polarizabilities (a.u.) of designed molecules. The calculation for βvec-1 is at a frequency of 0.00 EV(at static field quantities), βvec-2 is at 0.25EV(4959.37nm or 2016.38525 cm^{-1}), βvec-3 is at 0.50EV(2479.68 nm or 4032.77050cm^{-1})

	βvec-1	*βvec-2*	*βvec-3*		*βvec-1*	*βvec-2*	*βvec-3*
M-1	4657.027	4909.110	5829.227	MZ-1	3326.659	3466.212	3950.834
M-2	3861.663	4019.010	4564.544	MZ-2	4519.817	4735.687	5502.952
M-3	4343.073	4543.563	5250.803	MZ-3	2271.965	2347.452	2601.409
M-4	2409.036	2502.340	2824.121	MZ-4	5560.220	5839.286	6835.309
M-5	15004.307	16238.907	21118.555	MZ-5	7555.772	7998.989	9627.773
M-6	12999.309	13898.129	17344.717	MZ-6	12923.899	13762.576	16924.347
M-7	13141.464	14117.645	17902.137	MZ-7	8588.356	9094.666	10952.824
M-8	9015.785	9608.811	11840.335	MZ-8	12893.374	13743.877	16933.864
M-9	3496.536	3683.512	4363.602	MZ-9	4089.641	4289.198	4999.779
M-10	14730.528	15230.747	16925.246	MZ-10	6335.391	6455.917	6822.018
M-11	4162.340	4383.904	5181.618	MZ-11	2400.766	2499.666	2843.287
M-12	1922.946	2015.557	2344.763	MZ-12	5384.769	5703.137	6868.545
M-13	12408.405	13388.063	17263.505	MZ-13	9007.949	9556.523	11590.128
M-14	9593.435	10323.473	13208.302	MZ-14	12948.929	13955.401	17844.679
M-15	13343.343	14347.077	18243.986	MZ-15	10892.898	11588.392.	14183.412
M-16	7648.632	8162.785	10095.097	MZ-16	15322.562	16389.565	20437.286

The second-order polarizabilities (β) of designed molecules at different frequency are listed in table 3. Compared the N,N-dimethylaniline group (Rd1) and triphenylamine group (Rd2) in group MZ, the molecules with Rd2 have larger β values than that of molecules with Rd1 except the MZ-4 and MZ-12 . In the group M, the molecules with Rd2 have smaller β values than that of molecules with Rd1 except the M-7 and M-15. The Rd1 group can enhance the β values of molecules with one-heteroatom bridge, the Rd2 group can enhance the β values of molecules with three-heteroatom bridge. Considered the Ra1 and Ra2, the molecules with Ra2 have larger β values than that of molecules with Ra1 except the M-10 with M-14 and MZ-10 with Mz-14, which due to 2-(3-cyano-4,5,5-trimethylfuran-2-ylidene) malononitrile group (TCF Ra2) is a better electronic accepter than benzonitrile group (Ra1). Considered the frequency, the β values enhanced with the increasing of the frequency (βvec at 0.50EV>βvec at 0.25EV >βvec at 0.00 EV).