Synthesis, Crystal Structures, and Solid State Quadratic Nonlinear Optical Properties of a Series of Stilbazolium Cations Combined with Gold Cyanide Counter-Ion

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SUPPLEMENTARY INFORMATION

1-Description of the observed experimental effective susceptibilities

Because of the strong 1-dimensional character of the molecule with a dominating β_{zzz} component, we may assume that the dipolar molecule lies on a vertical mirror plane (pseudo-local symmetry) (see Figure 8). For the point group symmetry *m* (or *Cs* in Shoenflies notation) with XZ plane, the non-vanishing SHG tensor components are:[1]

$$\begin{bmatrix} XXX & XYY & XZZ & 0 & XXZ & 0 \\ 0 & 0 & 0 & YYZ & 0 & YYX \\ ZXX & ZYY & ZZZ & 0 & ZZX & 0 \end{bmatrix} \quad \text{(S1)}$$

The 1-dimensional character of the molecule contributes to components inside the XZ plane and non-zero terms are respectively ZZZ, ZXX and ZZX contributing to the nonlinear

[1] Verbiest, T.; Clays, K.; Rodriguez, V. *Second-order nonlinear optical characterizations techniques: An Introduction,* Chapter 1, CRC Press, New York, 2010.

polarization along Z (P_Z) and XXX, XZZ and XXZ contributing to the nonlinear polarization along X (P_X):

$$\begin{aligned} P_X &= d_{XXX}E_X^2 + d_{XZZ}E_Z^2 + 2d_{XXZ}E_X E_Z \\ P_Y &= 0 \\ P_Z &= d_{ZXX}E_X^2 + d_{ZZZ}E_Z^2 + 2d_{ZZX}E_X E_Z \end{aligned} \qquad \text{(S2)}$$

Hence for a collimated (unfocused) beam a response is expected along Z while no response along Y is expected.

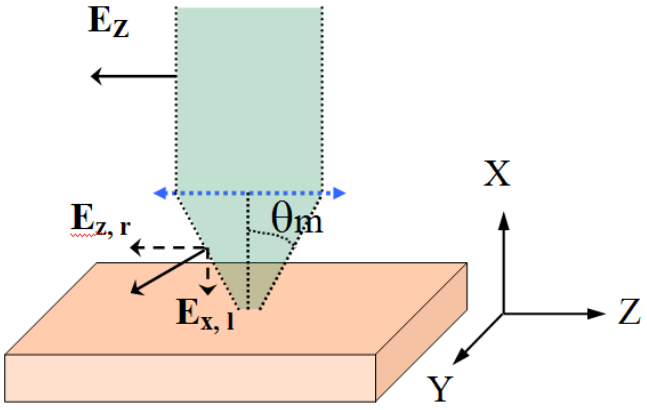

Figure SI-1: Splitting of an incoming polarized beam E_z into a transverse (or radial) $E_{z,r}$ and a longitudinal component $E_{x,l}$, by an objective of large NA. Note that the half-aperture angle, θ_m, is related to the NA.

As mentioned in the body text, in a μ-SHG experiment, the NLO interaction is confined into a small sample volume and defined by the DOF (Eq. 3). Due to the numerical aperture of the objective (NA=0.42) the interaction volume is almost ellipsoidal so that light propagation inside the material remains somewhat similar to the propagation expected in a classical SHG macroscopic experiment. The only difference lies in the large angular distribution of photons hitting the sample. Therefore, a polarized excitation (or response) transmitted through an objective gives two components (Figure SI-1). The most intense, is the component transverse (radially oriented) with respect to the incoming beam. The other is an extra longitudinal component along the direction of light propagation at the origin of weak signals which are however usually easy to observe in quadratic NLO.[17b] This longitudinal contribution increases with the NA of the objective. Therefore, the initial incident Z polarized

beam splits into radial Z and longitudinal X terms and the collected intensity I_{ZZZ} ($I_{//}$) and I_{YZZ} ($I_{\wedge}$) are related to $d_{eff}(ZZZ)$ and $d_{eff}(YZZ)$ respectively as follows:

$$\begin{aligned} d_{eff}(ZZZ) &= P_{Z,r}\cos(\theta_m) \quad + P_{X,l}\sin(\theta_m) \\ d_{eff}(YZZ) &= (P_Y = 0) \qquad + P_{X,l}\sin(\theta_m) \end{aligned} \tag{S3}$$

where θ_m is the half-aperture angle (Figure SI-1) and:

$$\begin{aligned} P_{X,l} = \; & d_{XXX}E_{X,l}^2 + d_{XZZ}E_{Z,r}^2 + 2d_{XXZ}E_{X,l}E_{Z,r} \\ & = \left(d_{XXX}\sin^2(\theta_m) + d_{XZZ}\cos^2(\theta_m) + 2d_{XXZ}\sin(\theta_m)\cos(\theta_m)\right)E^2 \\ P_{Z,r} = \; & d_{ZXX}E_{X,l}^2 + d_{ZZZ}E_{Z,r}^2 + 2d_{ZZX}E_{X,l}E_{Z,r} \\ & = \left(d_{ZXX}\sin^2(\theta_m) + d_{ZZZ}\cos^2(\theta_m) + 2d_{ZZX}\sin(\theta_m)\cos(\theta_m)\right)E^2 \end{aligned} \tag{S4}$$

Now, in a focused beam geometry, a response is (still) expected along Z ($d_{eff}(ZZZ)$) and the response along Y ($d_{eff}(YZZ)$) should be weak due to the extra longitudinal polarization $P_{X,l}$:

$$\begin{aligned} d_{eff}(ZZZ) = \; & \left(\begin{array}{l} d_{ZZZ}\cos^3(\theta_m) + d_{XXX}\sin^3(\theta_m) + 3d_{XZZ}\cos^2(\theta_m)\sin(\theta_m) \\ +3d_{XXZ}\sin^2(\theta_m)\cos(\theta_m) \end{array}\right)E^2 \\ d_{eff}(YZZ) = \; & \left(\begin{array}{l} \qquad\qquad d_{XXX}\sin^3(\theta_m) + \quad d_{XZZ}\cos^2(\theta_m)\sin(\theta_m) \\ +2d_{XXZ}\sin^2(\theta_m)\cos(\theta_m) \end{array}\right)E^2 \end{aligned} \tag{S5}$$

2-Estimation of the crystal 1-D susceptibility from the effective experimental susceptibilities

Following the orientation of 1-dimensional molecule in the crystal as sketched in Figure 8, the relationship between the molecular β_{xxx} component and the crystal (Laboratory) frame components d_{IJK} are:

$$\begin{aligned} d_{ZZZ} &= N\beta^*_{xxx}\sin^3(\theta) \\ d_{XXZ} &= N\beta^*_{xxx}\sin(\theta)\cos^2(\theta) \\ d_{XZZ} &= N\beta^*_{xxx}\sin^2(\theta)\cos(\theta) \\ d_{XXX} &= N\beta^*_{xxx}\cos^3(\theta) \end{aligned} \qquad \text{(S6)}$$

where β^*_{xxx} is the molecular component β_{xxx} corrected from local field effects. Taking now relations from equation S6 into equation S5 leads to the following simplified expressions:

$$\begin{aligned} \frac{d_{eff}(ZZZ)}{N\beta^*_{xxx}} &= \left(\sin(\theta)\cos(\theta_m)+\cos(\theta)\sin(\theta_m)\right)^3 E^2 \\ &= \sin^3(\theta+\theta_m) \\ \frac{d_{eff}(YZZ)}{N\beta^*_{xxx}} &= \cos(\theta)\sin(\theta_m)\left(\sin(\theta)\cos(\theta_m)+\cos(\theta)\sin(\theta_m)\right)^2 E^2 \\ &= \cos(\theta)\sin(\theta_m)\sin^2(\theta+\theta_m) \end{aligned} \qquad \text{(S7)}$$

These two equations are coupled. θ and θ_m cannot be determined independently from each other thereby. Finally we deduce from Equation S7:

$$\frac{d_{eff}(ZZZ)}{d_{eff}(YZZ)} = \frac{\sin(\theta+\theta_m)}{\cos(\theta)\sin(\theta_m)} = \frac{tg(\theta)}{tg(\theta_m)}+1 \qquad \text{(S8)}$$

or equivalently:

$$tg(\theta) = \left(\frac{d_{eff}(ZZZ)}{d_{eff}(YZZ)}-1\right)tg(\theta_m) \qquad \text{(S9)}$$

Since $d_{eff}(//,\perp) \propto \sqrt{I_{2\omega}(//,\perp)}$ we obtain the estimated numerical value:

$$tg(\theta) \approx \left(\sqrt{152.10^6/4.10^6}-1\right)\times tg(\theta_m) \approx 5.164 \times tg(\theta_m)$$

With NA=0.42 (Obj. 50x), we obtain $\theta_m \approx 25°$ in the air which induces an internal angle in the material $\theta_m \approx 15°$, assuming a refraction index $n_{crystal} \approx 1.6$. Taking this value as a maximum

limit, we obtain θ » 54° and since $N\beta^*_{xxx} = d_{eff}(ZZZ)/\sin^3(\theta+\theta_m)$ (Eq. S7) we obtain $d_{zzz} = N\beta^*_{xxx} \approx$ 4500 pm/V, which is very close to the effective value estimated from the crudest preliminary approximation (3660 pm/V). Considering now half this value, i.e. $\theta_m \approx 15°/2$, we deduce θ ≈ 34° and from (Eq. S7) we gain $d_{zzz} = N\beta^*_{xxx} \approx$ 12400 pm/V.

As a conclusion, in this tentative original method to quantify the susceptibility of the crystal measured at 1.064 µm, we estimate the dynamical value $d_{zzz}(-2\omega;\omega,\omega)$ ranges between 4500 pm/V and 12400 pm/V. Therefore using the two-level model (Eq. 4) with an absorption band maximum at 477 nm (Table 2) we obtain a dispersion factor of 6.38 and the static value $d_{zzz}(0;0,0)$ ranges between ~705 pm/V (~1.7 $\times 10^{-6}$ esu) and 1940 pm/V (~4.6 $\times 10^{-6}$ esu) which actually ranges quite well the calculated value 9.55 $\times 10^{-6}$ esu given in Eq. 9.

3-Atomic coordinates calculated by DFT at the B3LYP 6-31G level**
(Solvent: Acetonitrile)

DAMS$^+$

C	5.477114	7.108405	-6.591675
C	6.226698	6.981903	-5.398266
C	7.495594	7.611693	-5.373438
C	7.980473	8.313954	-6.456311
C	7.219705	8.437950	-7.656216
C	5.944493	7.808069	-7.686587
C	5.674820	6.236556	-4.298920
C	6.239494	6.014463	-3.074584
C	5.642675	5.257016	-2.009490
C	6.334223	5.112867	-0.778064
C	5.797582	4.393593	0.260370
N	4.585294	3.789888	0.146123
C	3.887083	3.904094	-1.016217
C	4.378592	4.612325	-2.082788
C	4.006128	3.062472	1.290817
N	7.697752	9.132282	-8.729747

C	6.900220	9.246119	-9.946697
C	9.010780	9.767638	-8.675595
H	6.306191	4.271732	1.208108
H	7.306707	5.570895	-0.640794
H	3.772497	4.655718	-2.978293
H	2.928203	3.403001	-1.047358
H	7.218078	6.430814	-2.853249
H	4.691303	5.813924	-4.496039
H	8.115652	7.547463	-4.484958
H	8.957061	8.774578	-6.383042
H	5.325246	7.870391	-8.571918
H	4.498481	6.639022	-6.649808
H	9.807307	9.033322	-8.506787
H	7.450878	9.833150	-10.679797
H	5.944454	9.748147	-9.755445
H	9.204293	10.264635	-9.624793
H	9.062061	10.520455	-7.880112
H	6.691178	8.262678	-10.384013
H	3.420947	3.748709	1.906668
H	3.365458	2.264484	0.918456
H	4.811875	2.631223	1.883064

$DEASH^{+}$

N	5.229699	7.248515	-6.269536
N	11.835604	6.792226	2.255527
C	6.401549	7.901907	-6.468421
H	6.533231	8.376148	-7.431849
C	7.345106	7.935553	-5.474043
H	8.274360	8.462645	-5.654413
C	7.119411	7.294453	-4.223620
C	5.870533	6.625332	-4.077282
H	5.612571	6.106981	-3.163182
C	4.956868	6.617078	-5.098883

H	3.997351	6.121532	-5.032301
C	8.134134	7.355231	-3.211882
H	9.033471	7.896311	-3.491602
C	8.045122	6.798474	-1.965002
H	7.132663	6.266088	-1.703121
C	9.030953	6.826313	-0.922028
C	10.295619	7.455441	-1.038441
H	10.570292	7.954569	-1.962290
C	11.210598	7.448397	-0.008502
H	12.166337	7.930185	-0.167062
C	10.927673	6.804770	1.234845
C	9.654821	6.176353	1.355895
H	9.369818	5.690002	2.279375
C	8.752617	6.191401	0.312098
H	7.790628	5.703526	0.446382
C	13.104375	7.527252	2.181733
H	12.946386	8.470173	1.652156
H	13.376785	7.799719	3.205388
C	14.240537	6.725308	1.538837
H	15.162206	7.315591	1.539366
H	14.004924	6.458612	0.504702
H	14.429230	5.800759	2.093120
C	11.601286	6.043112	3.496115
H	12.581017	5.745857	3.881083
H	11.074434	5.114193	3.263462
C	10.846987	6.845038	4.561840
H	10.730931	6.244943	5.469737
H	9.851804	7.135004	4.213000
H	11.393442	7.756062	4.824600
H	4.541632	7.230676	-7.012866

$DMASH^{+}$

C	5.372541	7.338970	-6.415202

C	6.173789	7.242769	-5.252311
C	7.375672	7.993991	-5.242544
C	7.750012	8.780737	-6.310483
C	6.937861	8.873071	-7.479694
C	5.729778	8.121116	-7.494964
C	5.736527	6.407838	-4.167860
C	6.368515	6.189782	-2.974695
C	5.885313	5.342375	-1.921991
C	6.649793	5.209254	-0.729272
C	6.223222	4.409585	0.300283
N	5.055081	3.729791	0.190655
C	4.282243	3.816182	-0.921905
C	4.669321	4.603225	-1.975174
N	7.306380	9.650790	-8.538111
C	6.457268	9.732523	-9.722692
C	8.550751	10.413456	-8.499534
H	6.773249	4.280541	1.223099
H	7.586082	5.743617	-0.620979
H	4.023203	4.642745	-2.842085
H	3.367821	3.237679	-0.917927
H	7.315508	6.682397	-2.773976
H	4.788595	5.904100	-4.347453
H	8.029880	7.959296	-4.377280
H	8.678215	9.333882	-6.249666
H	5.076105	8.154630	-8.356708
H	4.442963	6.777602	-6.460644
H	9.421436	9.757488	-8.383703
H	6.920740	10.399608	-10.447476
H	5.464772	10.129233	-9.478902
H	4.750989	3.142487	0.957920
H	8.661019	10.960383	-9.434445
H	8.553542	11.138956	-7.677552
H	6.330035	8.751015	-10.194179

MPSH$^+$

O	0.695905	12.005147	10.956637
N	10.052108	5.148162	5.644145
N	0.979375	9.365958	9.662948
C	9.790635	5.336795	6.962977
H	10.564159	5.031316	7.655075
C	8.600365	5.886302	7.362490
H	8.433015	6.014565	8.423731
C	7.618570	6.269912	6.404879
C	7.951891	6.044952	5.039765
H	7.251024	6.312279	4.257869
C	9.155945	5.491987	4.685740
H	9.448407	5.306080	3.660790
C	6.347943	6.850959	6.730309
H	5.707068	7.066244	5.880223
C	5.911271	7.142870	7.993645
H	6.575202	6.929321	8.829135
C	4.650475	7.714672	8.375116
C	4.388819	7.958650	9.745238
H	5.151313	7.707674	10.478104
C	3.199918	8.504315	10.184326
H	3.060610	8.667387	11.245119
C	2.168871	8.840906	9.262049
C	2.426983	8.596988	7.879700
H	1.673338	8.838197	7.140920
C	3.623075	8.056630	7.460278
H	3.766276	7.891206	6.397241
C	0.600041	9.591072	11.071074
C	-0.940108	9.578865	11.021666
H	-1.295571	8.549576	11.134861
H	-1.378744	10.176576	11.824062
C	-1.281631	10.113500	9.621896
H	-1.271396	11.204544	9.629264

H	-2.257949	9.776069	9.265995
C	-0.144972	9.583648	8.736787
H	-0.415311	8.635008	8.253789
H	0.128244	10.293444	7.948560
C	1.195927	10.878673	11.653188
H	0.929584	10.931533	12.721866
H	2.294870	10.850937	11.591236
C	1.207248	13.227456	11.461024
H	0.770525	14.032458	10.866077
H	2.302936	13.273637	11.375888
H	0.936042	13.375095	12.516739
H	0.967939	8.763134	11.687648
H	10.938266	4.740393	5.369961