Nonlinear optical properties of intriguing Ru σ-acetylides complexes and the use of a photocrosslinked polymer as a springboard to obtain SHG active thin films.

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Table S1. Calculated electronic properties for complexes 1' and 2' at different levels of theory: transition energy (ω_{01}) and dipole moment (μ_{01}^z), ground (μ_{00}^z) and excited (μ_{11}^z) state dipole moment, first ($\beta_{zzz}(-2\omega;\omega,\omega)$) and second ($\gamma_{zzzz}(-2\omega;\omega,\omega,0)$) hyperpolarisabilities relevant to compute the EFISH contributions (eqn 1), cubic diagonal term ($\gamma_{zzzz}(-3\omega;\omega,\omega,\omega)$) relevant to THG experiments. The sum over states has been implemented according to Eqn. (22), (30) and (29) from Ref. [1], respectively. Superscript T and X stand for Taylor series and phenomenological convention, respectively. The bar (subscript *av*) indicates orientational averaging. We stress that according to Ref. [2], $\gamma^X(-2\omega;\omega,\omega,0)=\frac{1}{4}\gamma^T(-2\omega;\omega,\omega,0)$, while $\gamma^X(-3\omega;\omega,\omega,\omega)=\frac{1}{24}\gamma^T(-3\omega;\omega,\omega,\omega)$. Eq and NEq indicate that the TD-DFT calculations have been performed under equilibrium (all solvent degrees of freedom are relaxed) and non-equilibrium conditions, respectively.[3] The latter is a priori more relevant to the experiments conducted in this study.

Compound	1'				2'			
Geometry	DCM	DCM	DCM	gas	DCM	DCM	DCM	gas
Properties	DCM(Eq)	DCM(NEq)	gas	gas	DCM(Eq)	DCM(NEq)	gas	gas
ω_{01} (eV)	*2.264*	2.367	2.597	2.639	*2.307*	2.408	2.662[#]	2.634
μ_{01}^z (D)	*-14.96*	-14.08	-10.20	-11.82	*-16.00*	-15.22	-13.73[#]	-12.91
μ_{00}^z (D)	*+5.23*	+5.23	+3.18	+3.01	*+12.03*	+12.03	+8.91	+9.01
μ_{11}^z (D)	*-4.31*	-5.72	-3.57	-6.44	*+3.73*	+2.09	+0.71[#]	+0.56
$\beta_{zzz}^T(-2\omega;\omega,\omega)$ (10^{-28} esu)	*-8.03*	-7.03	-1.69	-3.03	*-2.59*	-7.05	-3.46	-3.25
$\gamma_{zzzz}^T(-2\omega;\omega,\omega,0)$ (10^{-33} esu)	*-12.49*	+0.59	-1.37	+0.58	*-7.13*	-9.58	-6.23	-3.56
$\gamma_{zzzz}^T(-3\omega;\omega,\omega,\omega)$ (10^{-33} esu)	*-36.54*	-4.05	-3.33	-1.51	*-11.29*	-24.85	-12.71	-8.33
$\bar{\gamma}_{av}^T(-2\omega;\omega,\omega,0)$ (10^{-33} esu)	*-2.50*	+0.12	-0.27	+0.12	*-1.43*	-1.92	-1.25	-0.71
$\bar{\bar{\gamma}}_{av}^T(-3\omega;\omega,\omega,\omega)$ (10^{-33} esu)	*-7.31*	-0.08	-0.67	-0.30	*-2.26*	-4.97	-2.54	-1.67
$\bar{\gamma}_{av}^T(-3\omega;\omega,\omega,\omega)/\bar{\bar{\gamma}}_{av}^T(-2\omega;\omega,\omega,0)$	*+2.92*	-0.67	+2.48	-2.50	*+1.58*	+2.59	+2.03	+2.35
$(\omega_{01}-2\omega)/(\omega_{01}-3\omega)$	*+3.07*	+2.56	+2.00	+1.94	*+2.82*	+2.42	+1.91	+1.95
$\beta_{zzz}^X(-2\omega;\omega,\omega)$ (10^{-28} esu)	*-2.03*	-1.76	-0.42	-0.76	*-0.65*	-1.76	-0.87	-0.81
$\frac{\mu_{00}^z\beta_{zzz}^X(-2\omega;\omega,\omega)}{5kT}$ (10^{-33} esu)	*-5.10*	-4.47	-0.65	-1.11	*-3.78*	-10.30	-3.75	-3.56
$\gamma_{zzzz}^X(-2\omega;\omega,\omega,0)$ (10^{-33} esu)	*-3.12*	+0.15	-0.34	+0.14	*-1.78*	-2.39	-1.56	-0.89

$\bar{\gamma}^{X}_{EFISH}$ (10^{-33} esu)	*-0.62*	+0.03	-0.07	+0.03	*-0.36*	-0.48	-0.31	-0.18
$\gamma^{TOT,X}_{EFISH}$ (10^{-33} esu)	*-5.72*	-4.44	-0.72	-1.08	*-4.14*	-10.78	-4.06	-3.74
$\bar{\gamma}^{X}_{THG}$ (10^{-33} esu)	*-0.30*	-0.003	-0.03	-0.01	*-0.09*	-0.20	-0.11	-0.07

the bright excited state is the second one

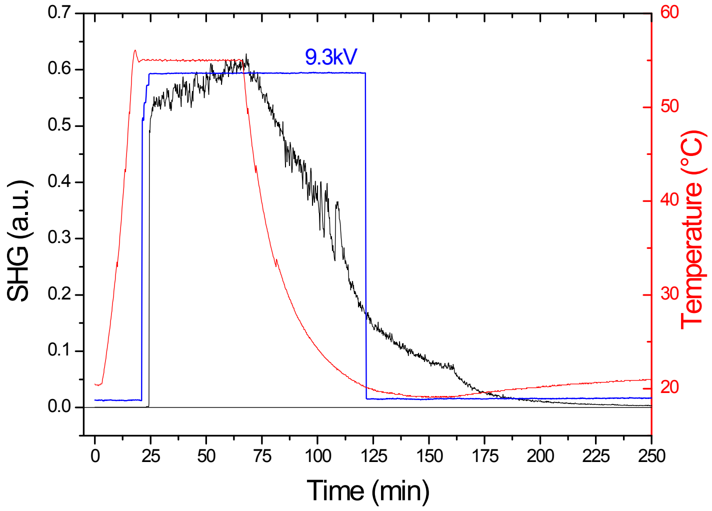

Figure S1. In situ corona-wire poling dynamic of a PS film containing complex **2**.

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