Electronic supplementary information (ESI)

Synthesis of nonlinear optical chromophores with isophorone-derived bridges for enhanced thermal stability and electro-optic activity

Fenggang Liu [a]*, Songmin Mo [a], Zhaofen Zhai [a], Meishan Peng [a], Shuangke Wu [a], Chunling Li [a], Canwen Yu [a] and Jianpeng Liu [a]

[a]*School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China. E-mail address: liufg6@gzhu.edu.cn*

1. Optical properties

Table s1 Optical Properties data of the chromophore.

Cmpd	λ_{max}[a]	λ_{max}[b]	λ_{max}[c]	λ_{max}[d]	λ_{max}[e]
J1	753	666	688	688	688
J2	750	666	691	678	681
J3	762	667	688	689	689
J4	763	667	688	688	688

[a, b, c, d, e] (nm) was measured in chloroform, dioxane, toluene, acetone and acetonitrile , respectively.

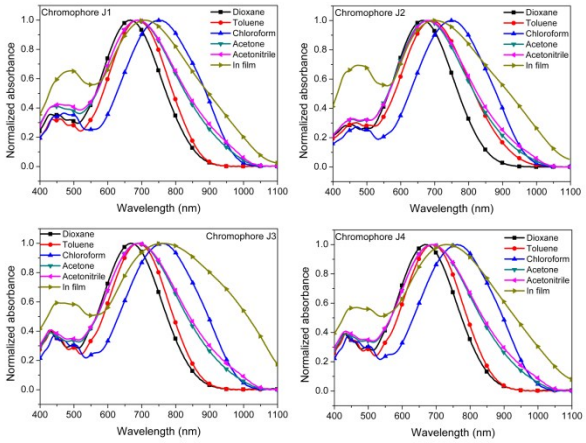

Fig. S1 UV-Vis absorption spectra of chromophores J1-J4 in five kinds of aprotic solvents with varying dielectric constants and in films.

2. Summary of DFT data

Table s2 The Molecular Orbital Composition (%) in the Ground State for Chromophores J1-J4.

Cmpd	J1		J2		J3		J4	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
donor	64.50%	13.39%	55.06%	17.21%	64.45%	13.50%	65.18%	13.28%
π bridge	23.88%	40.35%	26.25%	40.50%	22.70%	39.29%	22.27%	39.33%
acceptor	11.62%	46.27%	15.74%	41.71%	11.15%	45.97%	10.84%	46.16%
IGs			2.95%	0.57%	1.70%	1.24%	1.71%	1.23%

The molecular orbital composition was calculated using Multiwfn program with Ros-Schuit (SCPA) partition.

3. Optimized structures of chromophores

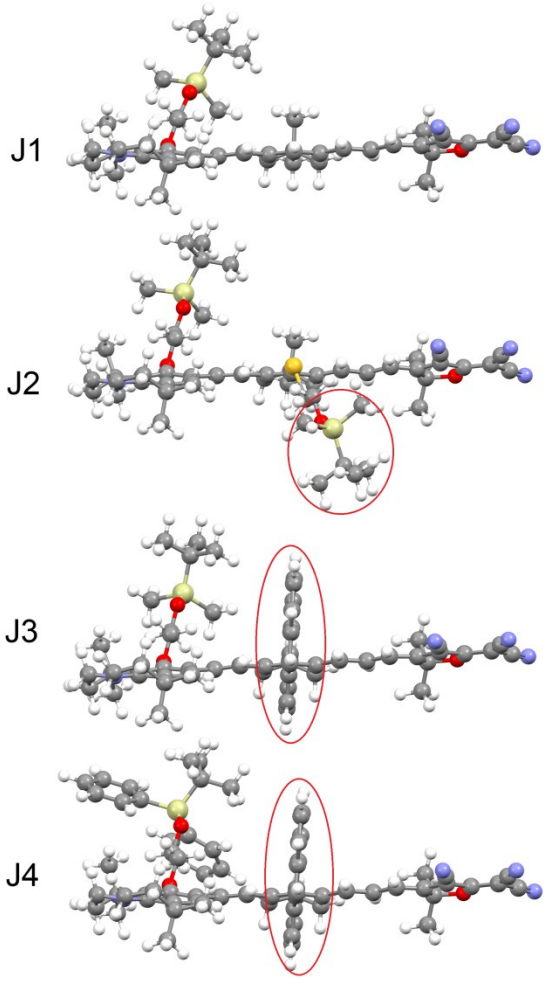

Fig. s2 Optimized structures of chromophores J1-J4.

4. Structure of chromophores A, A1, C, FLD1 and FLD4 and their electro-optic coefficients.

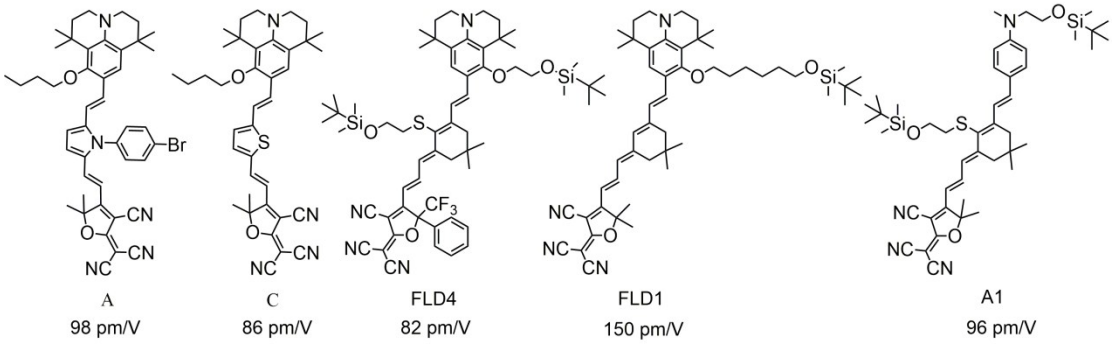

Fig. S3 Structure of chromophores A, A1, C, FLD1 and FLD4 and their electro-optic coefficients.[1-3]

5. Device Fabrication, poling and Testing.

Dibromomethane was dried over calcium chloride for several days then collected via vacuum distillation before use. ITO glass parameters: thickness = 45 nm; surface resistivity ≤ 100 ohms/square; transmission ≥ 85% at 1300-1500 nm.

Solutions of 8-10% weight EO material in dibromomethane were prepared and sonicated for 30min to dissolve, filtered through a 0.2 μm PTFE filter, and spin cast onto ITO/glass substrates. EO films were spin cast in three stages: 550 rpm for 5 seconds, 900 rpm for 30 seconds, followed immediately by 1500 rpm for 25seconds. The films were then dried in a vacuum oven at 60 ˚C overnight. The thickness of the EO film was then measured to be around 1-2 μm. Finally, patterned gold electrodes were deposited on top of the films by vacuum coating machine to complete the film device.

In general, for EO films，the electric field poling is conducted by applying an electric field at room temperature, heating the sample to its T_g and holding at that temperature for a few minutes (~10) until molecular orientation is complete, cooling to room temperature, and then remove the electric field. After poling and cooling to near room temperature, electro-optic coefficients for the poled films were measured using the Teng–Man technique on a custom apparatus at 1310 nm.[4]

Reference

1. F. Liu, H. Wang, Y. Yang, H. Xu, M. Zhang, A. Zhang, S. Bo, Z. Zhen, X. Liu and L. Qiu, *Journal of Materials Chemistry C*, 2014, **2**, 7785-7795.
2. F. Liu, H. Xu, H. Zhang, L. Chen, J. Liu, S. Bo, Z. Zhen, X. Liu and L. Qiu, *Dyes and Pigments*, 2016, **134**, 358-367.
3. F. Liu, S. Chen, S. Mo, G. Qin, C. Yu, W. Zhang, W.-J. Shi, P. Chen, H. Xu and M. Fu, *Journal of Materials Chemistry C*, 2019, **7**, 8019-8028.
4. H. Xu, F. Liu, D. L. Elder, L. E. Johnson, Y. de Coene, K. Clays, B. H. Robinson and L. R. Dalton, *Chemistry of Materials*, 2020, **32**, 1408-1421.