Supporting information for

# Poling Efficiency Enhancement of Tethered Binary Nonlinear Optical Chromophores for Achieving Ultrahigh n<sup>3</sup>r<sub>33</sub> Figure-of-Merit of 2601 pm/V

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## Measurement of thin film absorption spectra before and after poling

UV-vis-NIR spectra of EO films were obtained on a Perkin-Elmer Lambda-9 spectrophotometer. For the measurement, the top gold electrode of poled films was etched off by  $KI/I_2$  gold etchant. The depoled films were prepared by annealing the poled films at 110 °C for 10 min.



Fig. S1 Normalized absorption of C1, C2, C3 and compound 5 in chloroform.



Fig. S2 Absorption of C1/PMMA before and after different poling condition.



**Fig. S3** The third Legendre polynomials  $(L_3(u))$  as a function of order parameter, in which the mean field describing intermolecular interactions is assumed to be isotropic for the treatment of poled polymers. (D. M. Burland, R. D. Miller, and C. A. Walsh, "Second-order nonlinearity in poled-polymer systems", *Chemical Reviews* 94, 31-75 (1994)).

#### Measurement of thermal simulated discharge (TSD) current

For each test, the two electrodes of freshly poled EO polymer films were connected to a Keithley 617 electrometer in a short circuit configuration and placed into a closed slot on the programmable Mettler FP82 hot plate. The sample was heated from 30 °C to 120 °C at a constant rate of 5 °C/min. The discharge current was monitored and recorded.



Fig. S4 TSD spectra of poled C3/PMMA films under different applied electric field.



Fig. S5 TSD spectra of poled C2/PMMA films under different applied electric field.

#### Measurement of refractive index of C1 film

Optical characterisation was performed using a Metricon 2010/M prism coupler. The analysis was carried out at 1300 nm wavelengths using a prism of index 2.865 and effective modal index range of 1.55-2.45 (Metricon 200-P-2). The Guided-wave mode spectra of unpoled **C1** glass film before poling showed two guided modes of TE and TM polarization. The TM and TE refractive indices were measured to be 2.04 and 2.12, respectively.



Fig. S6 Guided-wave mode spectra of a C1 monolithic thin film on glass substrate by prism coupler. The film thickness is  $0.80 \mu m$ .

### Measurement of optical properties of molecular glass C1 by spectroscopic ellipsometry

The spectroscopic ellipsometer (M2000, J. A. Woollam) was used to measure the ellipsometric parameters,  $\Psi(\lambda)$  and  $\Delta(\lambda)$ , of C1 molecular glass films on the glass substrate at the wavelengths from 230 nm to 1600 nm. The incidence angles were set at 55°, 65° and 75°. The data analysis is based on the software CompletedEASE of the system to obtain the *n*, *k* values of the film.



Fig. S7 Refractive indices (n) and extinction coefficients (k) of molecular glass C1 measured by variable angle spectroscopic ellipsometry (VASE).

## Temporal stability measurement of poled EO films

The  $r_{33}$  values of poled films were measured using Teng–Man simple reflection technique at the wavelength of 1.3 µm. The poled films were then kept at 80 °C in the oven, and were taken to Teng-Man reflection measurement at different time intervals. The temporal alignment stability study of poled films was evaluated on by measuring the  $r_{33}$  values and comparing with that of freshly poled samples.



Fig. S7 Temporal stability of a poled C1 monolithic glass film at 80 °C in air for 100h.



<sup>1</sup>H NMR spectrum of C1

