

Supplementary Information

Twistable Dipolar Aryl Rings as Electric-field Actuated Conformational Molecular Switches

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S1. Estimates of switching times

In order to estimate the switching times for the three biphenyl systems considered, we first obtain the torque (τ) required to twist the substituted aryl ring in each case via the definition $\tau = \frac{dW}{d\theta}$, where W is the work done in twisting the aryl ring. Assuming that $dW = dE_{tot}$, we obtain an estimate of $\tau(\theta)$ from the following numerical derivative.

$$\tau(\theta) = \frac{E_{tot}(\theta) - E_{tot}(\theta - \Delta\theta)}{\Delta\theta}$$

To evaluate the time taken for a moderate applied E-field of 3.6×10^7 V/cm to twist a substituted aryl to the energy minima from a displaced angle, we use the angular range from 35° (approx. θ of the energy minima) from 60° (see Fig. S1a). Within the angle range 20° - 60° the acceleration is approximately linear (see Fig. S1a) which allows us to use the following differential equation:

$$\ddot{\theta} = k\theta + a$$

Where we use:

$$\frac{\tau}{I} = \ddot{\theta}$$

where I is the constant moment of inertia of the twisting aryl ring about its twisting axis.

The differential equation can be solved analytically to give the general solution

$$\theta(t) = c_1 e^{\sqrt{k}t} + c_2 e^{-\sqrt{k}t} - \frac{a}{k}, \text{ with } c_1 = \frac{1}{2} \left(\theta_0 + \frac{a}{k} + \frac{\dot{\theta}_0}{\sqrt{k}} \right) \text{ and } c_2 = \frac{1}{2} \left(\theta_0 + \frac{a}{k} - \frac{\dot{\theta}_0}{\sqrt{k}} \right)$$

Assuming the ring starts from rest at 60° we can use the following initial conditions to estimate $\theta(t)$ from 60° to 35° .

$$\theta_0 = 60^\circ, \quad \dot{\theta}_0 = 0$$

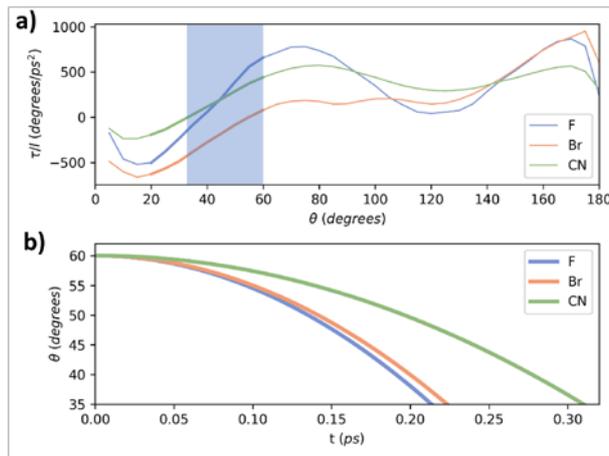


Fig. S1. a) Angular acceleration for each functionalised biphenyl in presence of 3.6×10^7 V/cm F_x as a function of θ . The thicker lines denote the linear acceleration range used to derive the differential equation. The shaded region indicates the 25° range used to obtain the timings. b) Integrated θ as function of time.

S2 Energetic contributions due to permanent and induced dipole interactions with the applied E-field

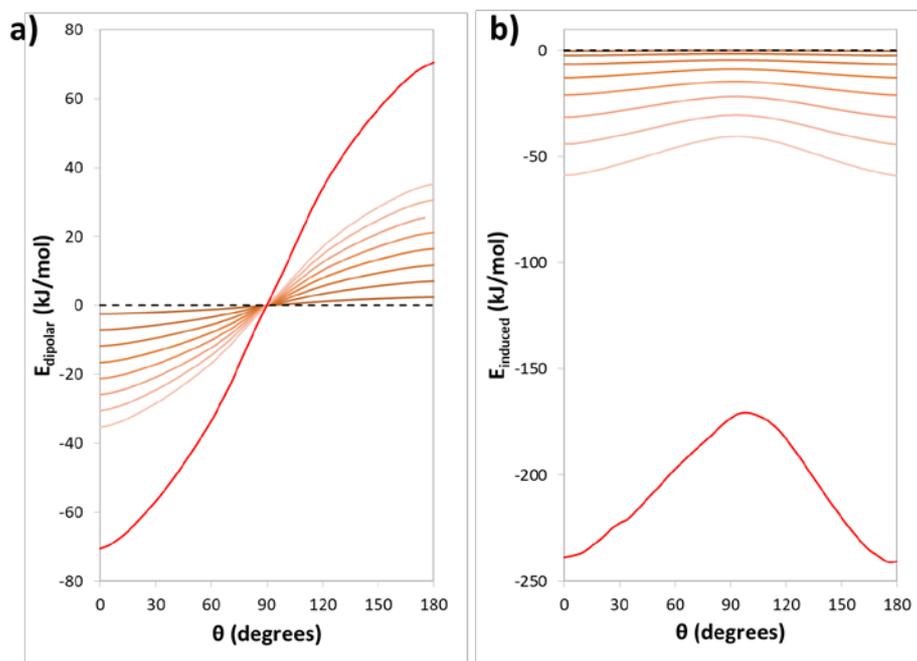


Fig. S2a. Dibromo system: a) Energy contribution due to the permanent dipole (second term in equation 1, main text). c) Energy contribution due to the induced dipole (third and higher order terms in equation 1).

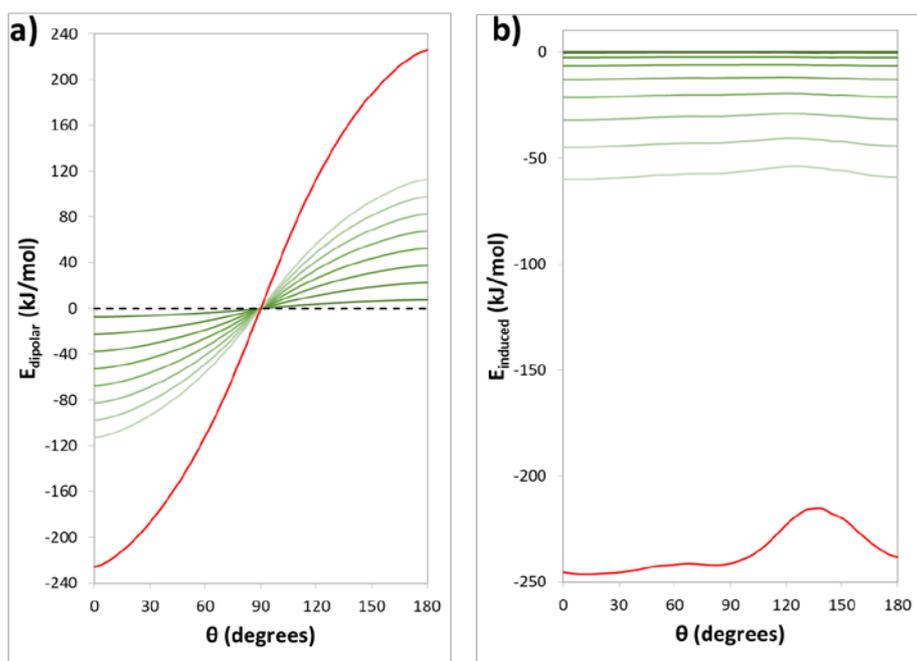


Fig. S2b. Dinitrile system: a) Energy contribution due to the permanent dipole (second term in equation 1, main text). b) Energy contribution due to the induced dipole (third and higher order terms in equation 1).

S3. Energetic contribution of the induced dipole on E_{rel}

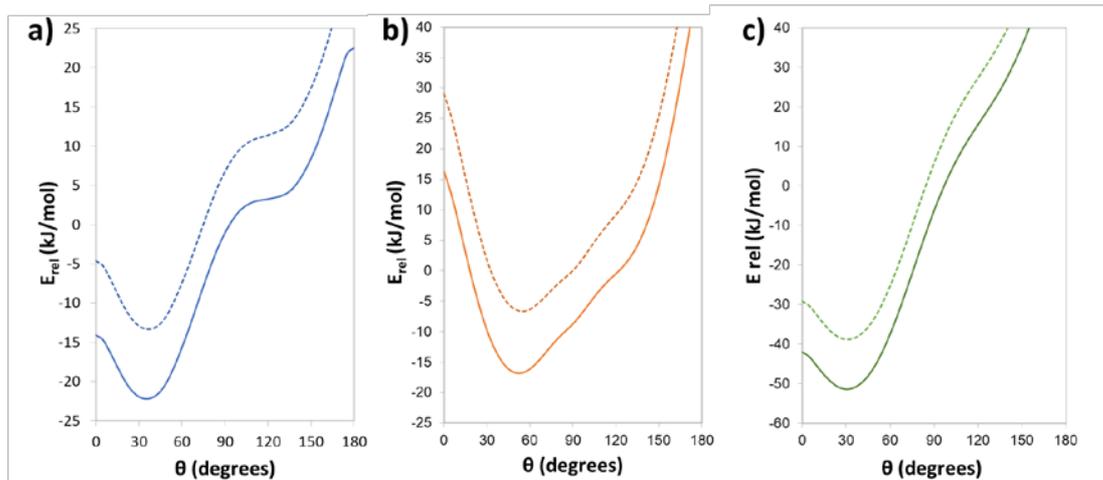


Fig. S3. E_{rel} curves (solid lines) and E_{rel} minus the third and higher order terms in equation 1 of the main text (dashed lines) for the: a) difluoro system, b) dibromo, and c) dinitrile systems.

S4. Selected virtual orbitals for the di-fluoro biphenyl system

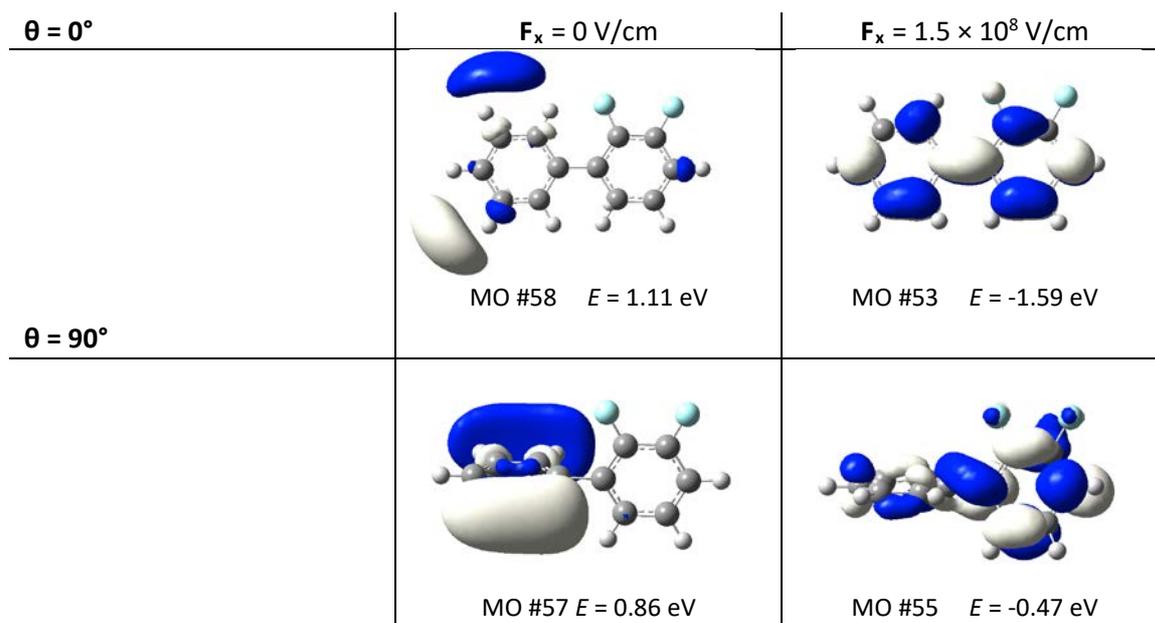


Figure S4. Selected virtual orbitals for the difluoro biphenyl system for $\theta = 0^\circ$ and $\theta = 90^\circ$, as obtained at zero E-field and at the highest field employed in this study. Note that the LUMO of this system is the molecular orbital #50.