Supporting Information for:

Phenalenyls as tunable excellent molecular conductors and switchable spin filters

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S1 Two-probe relaxations

The structure relaxations for the two-probe transport systems were carried out with the Vienna ab initio simulation package (VASP).[S1,S2] We used the projector augmented wave potentials[S3] with the Perdew-Burke-Enerzerhof generalized gradient approximation (PBE-GGA)[S4] with the D3[S5] empirical correction to include dispersion. The energy cutoff was 400 eV and a $2 \times 2 \times 1$ Γ-centered k-point grid was used. The relaxations were continued until forces on atoms were less than 0.02 eV/Å(for those atoms that were not frozen; see below).

The radicals and the naphthalene molecule were relaxed between Au electrodes as shown in Fig. S1a. First, the optimal electrode-electrode separation, d, was determined by a series of relaxations for the 1,3-DAPLY system. This was accomplished by freezing the atoms in the shaded regions to their bulk positions and allowing all other atoms to fully relax. Once the optimal electrode-electrode separation was found for 1,3-DAPLY, the distance was fixed and all other radicals and naphthalene were relaxed in a similar manner (with the same d for all systems).

The two-probe structures were created by extending the Au electrodes in either direction to build the system shown in Fig. S1b. We calculate the spin transport properties of these systems using the NEGF-DFT code Nanodcal,[S6,S7] which employs the retarded Green's function,

$$G(E) = [ES - H - \Sigma_{\mathrm{L}} - \Sigma_{\mathrm{R}}]^{-1}, \tag{S1}$$

where H and S are the Hamiltonian and overlap matrices for the central region of the two-probe structure, calculated by DFT. $\Sigma_{\mathrm{L,R}}$ are self-energies that account for the effect of the left/right electrodes on the central region; these are complex quantities with their real part representing a shift in the energy levels and their imaginary part representing the broadening, which can also be represented as the linewidth matrix, $\Gamma_{\mathrm{L,R}} = i(\Sigma_{\mathrm{L,R}} - \Sigma_{\mathrm{L,R}}^{\dagger})$. The self-energy is calculated within the NEGF-DFT formalism by an iterative technique.[S8]

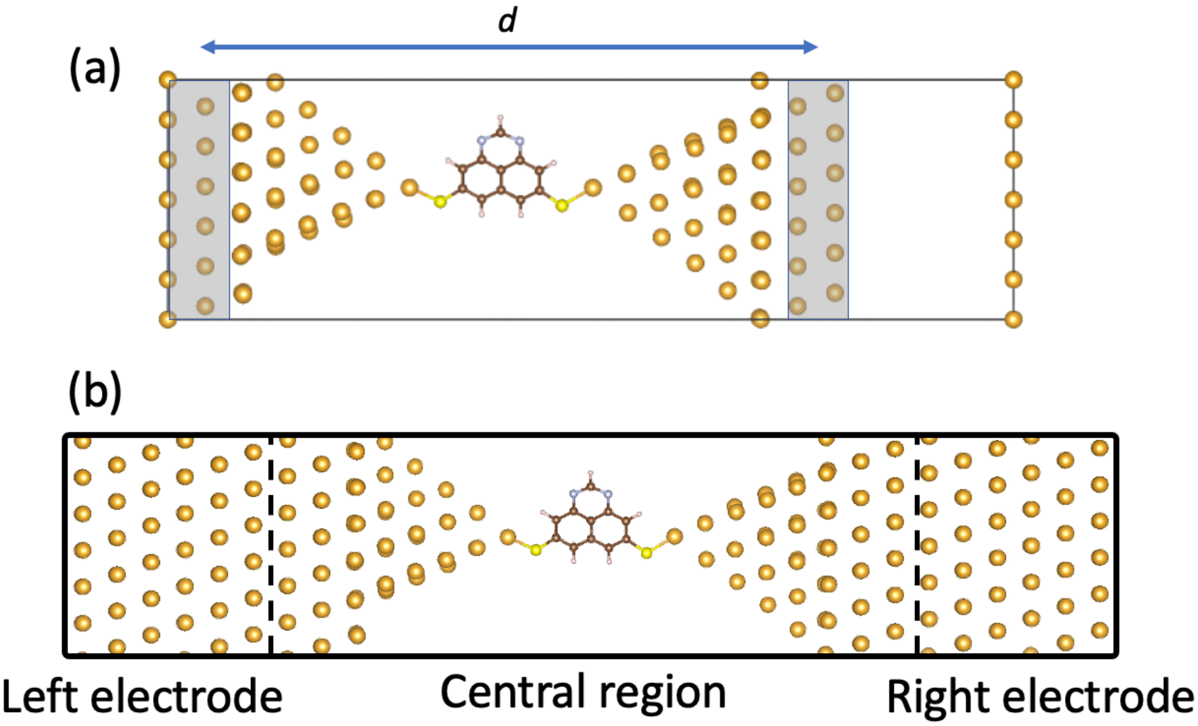

Figure S1: The two-probe structure relaxations were carried out on the system shown in (a), with the Au atoms in the shaded region being frozen while all other atoms being allowed to relax while minimizing the energy with respect to distance, d. The resulting minimum energy structure was used to build the two-probe structure for the electron transport calculations, shown in (b).

The electronic density matrix can be calculated from these quantities as,

$$\rho = \frac{1}{2\pi}\int_{-\infty}^{\infty}[f(E,\mu_{\mathrm{L}})G\Gamma_{\mathrm{L}}G^{\dagger} + f(E,\mu_{\mathrm{R}})G\Gamma_{\mathrm{R}}G^{\dagger}]dE, \tag{S2}$$

where $\mu_{\mathrm{L,R}}$ are the electrochemical potentials of the left and right electrodes and the Fermi-Dirac function describes the probability of occupying a single-particle orbital with a given energy at a specified electrochemical potential. The bias voltage between the two electrodes is given by, $eV_{\mathrm{b}} = \mu_{\mathrm{L}} - \mu_{\mathrm{R}}$. The density obtained from the above equation is used in a subsequent NEGF-DFT iteration step and the cycle is repeated until self-consistency is achieved in terms of the Hamiltonian and electron density.

The transmission coefficient is then obtained from the Green's function,

$$T(E, V_\mathrm{b}) = \mathrm{Tr}(\Gamma_\mathrm{L} G \Gamma_\mathrm{R} G^\dagger), \tag{S3}$$

which represents the probability that an electron with a given energy, E, transmits from one electrode through the central region into the other electrode. This quantity can be obtained for an electron having spin σ, and the spin-resolved current can be obtained by integrating the transmission function in the bias window with the Landauer-Büttiker equation,[S9]

$$I_\sigma(V_\mathrm{b}) = -\frac{e}{h} \int_{\mu_\mathrm{L}}^{\mu_\mathrm{R}} T_\sigma(E, V_\mathrm{b})[f(E, \mu_\mathrm{L}) - f(E, \mu_\mathrm{R})] dE. \tag{S4}$$

S2 Spin density, MOs, Transmission

The figures in this section show the spin density distribution over the isolated radicals, the spin-resolved molecular orbitals (MOs) with their corresponding energies, and transmission spectra with transmission peaks assigned to their corresponding MOs.

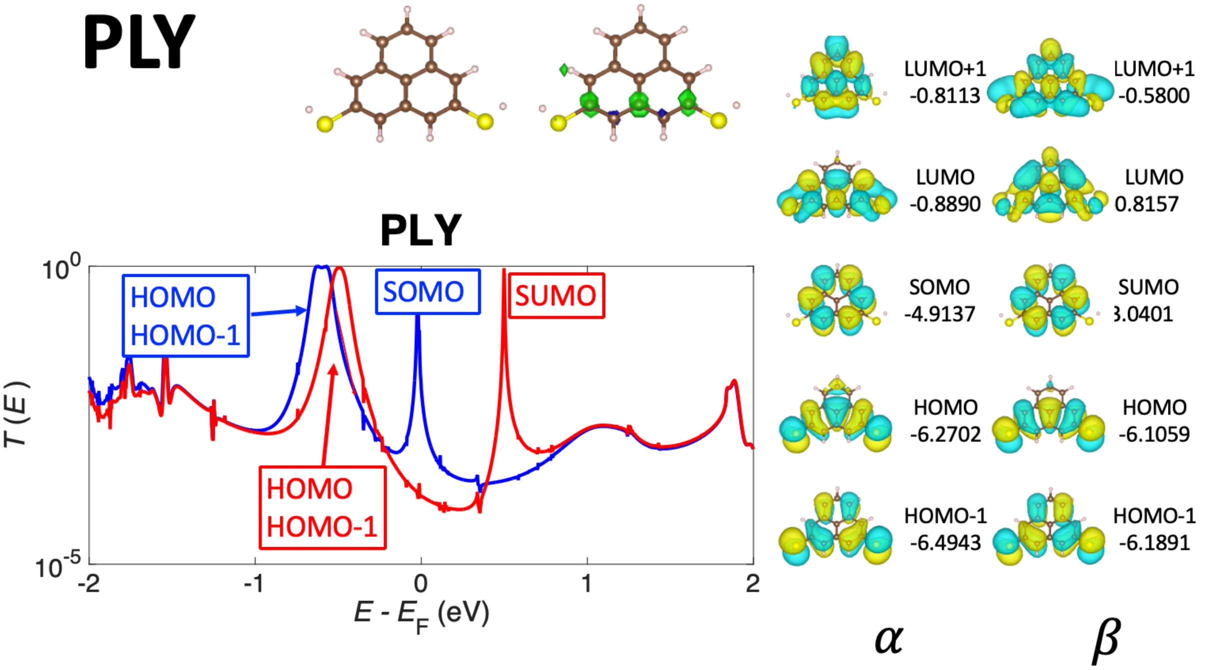

Figure S2: PLY: spin density (top-middle), α and β MOs of isolated molecule with corresponding energies (eV) (right), and spin-resolved transmission spectra (α in blue, β in red) with assigned MOs responsible for transmission peaks (bottom left). The peak assignments were obtained by using the approach demonstrated in Fig. S5.

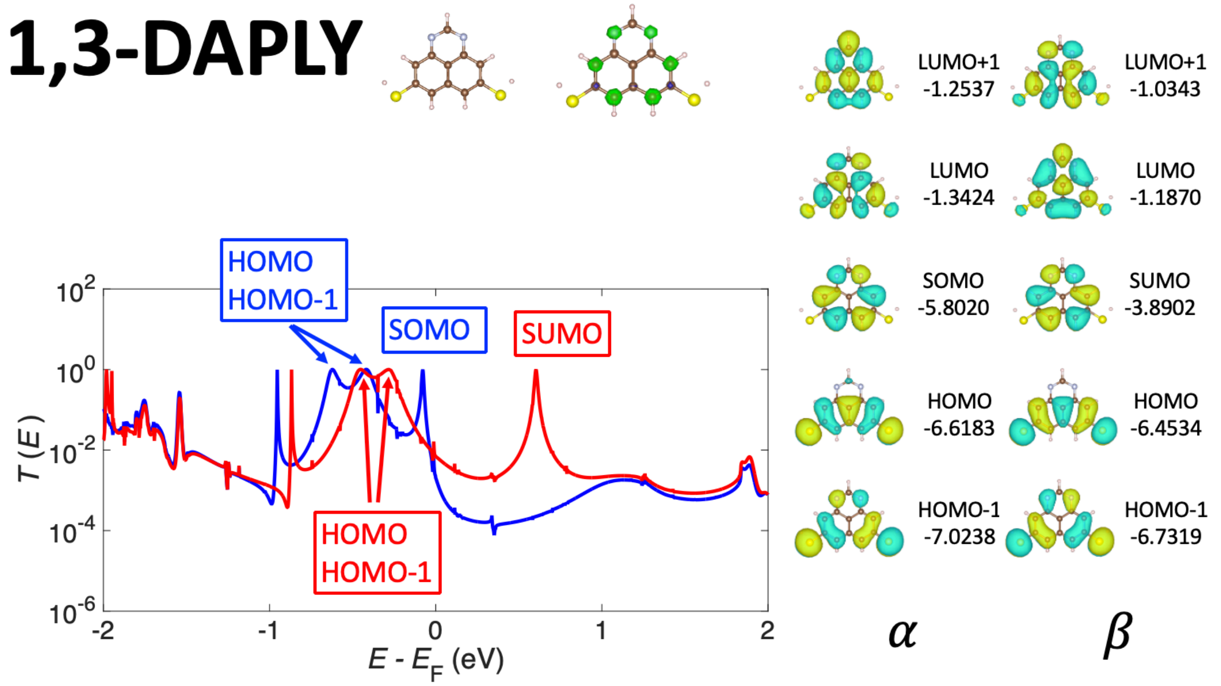

Figure S3: 1,3-DAPLY: spin density (top-middle), α and β MOs of isolated molecule with corresponding energies (eV) (right), and spin-resolved transmission spectra (α in blue, β in red) with assigned MOs responsible for transmission peaks (bottom left). The peak assignments were obtained by using the approach demonstrated in Fig. S5.

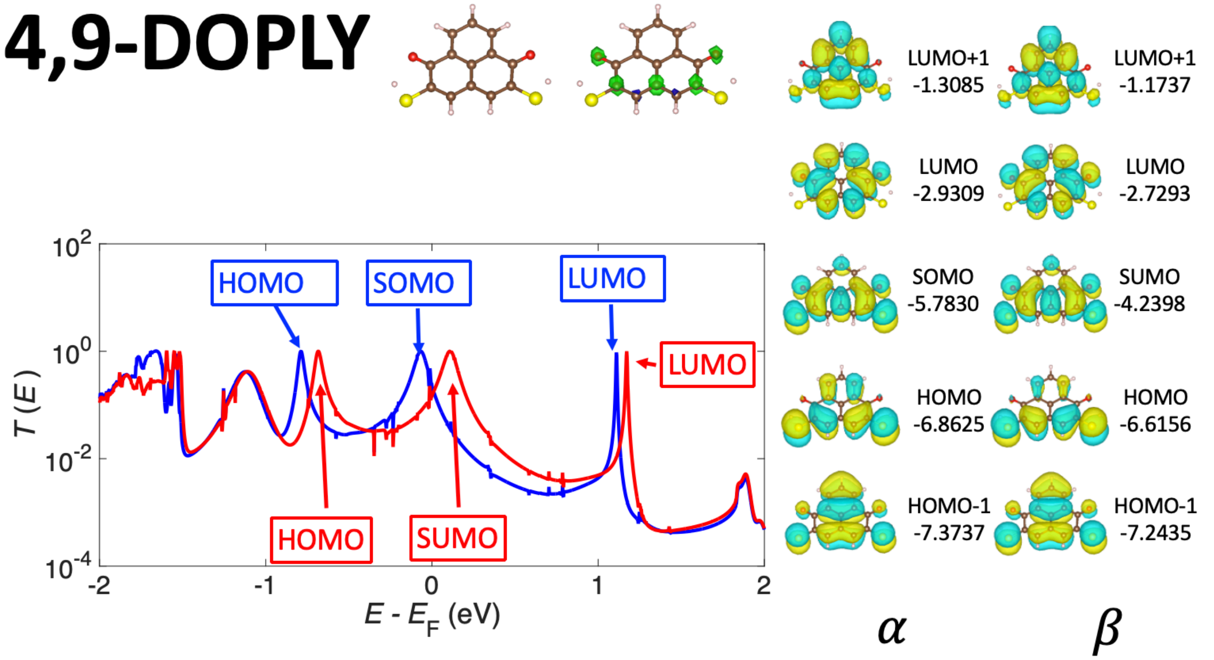

Figure S4: 4,9-DOPLY: spin density (top-middle), α and β MOs of isolated molecule with corresponding energies (eV) (right), and spin-resolved transmission spectra (α in blue, β in red) with assigned MOs responsible for transmission peaks (bottom left). The peak assignments were obtained by using the approach demonstrated in Fig. S5

1,3-DA-4,9-DOPLY

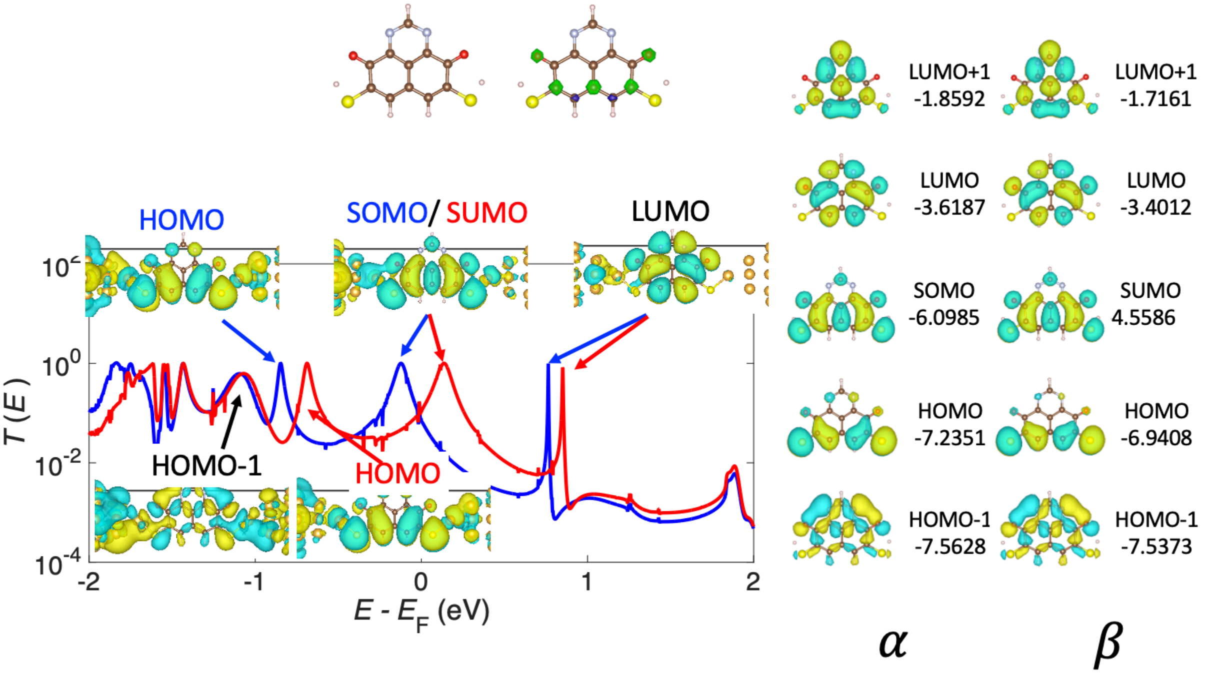

Figure S5: 1,3-DA-4,9-DOPLY: spin density (top-middle), α and β MOs of isolated molecule with corresponding energies (eV) (right), and spin-resolved transmission spectra (α in blue, β in red) with assigned MOs responsible for transmission peaks (bottom left). The scattering states are shown for relevant transmission peaks, which can be assigned to MOs by visual comparison.

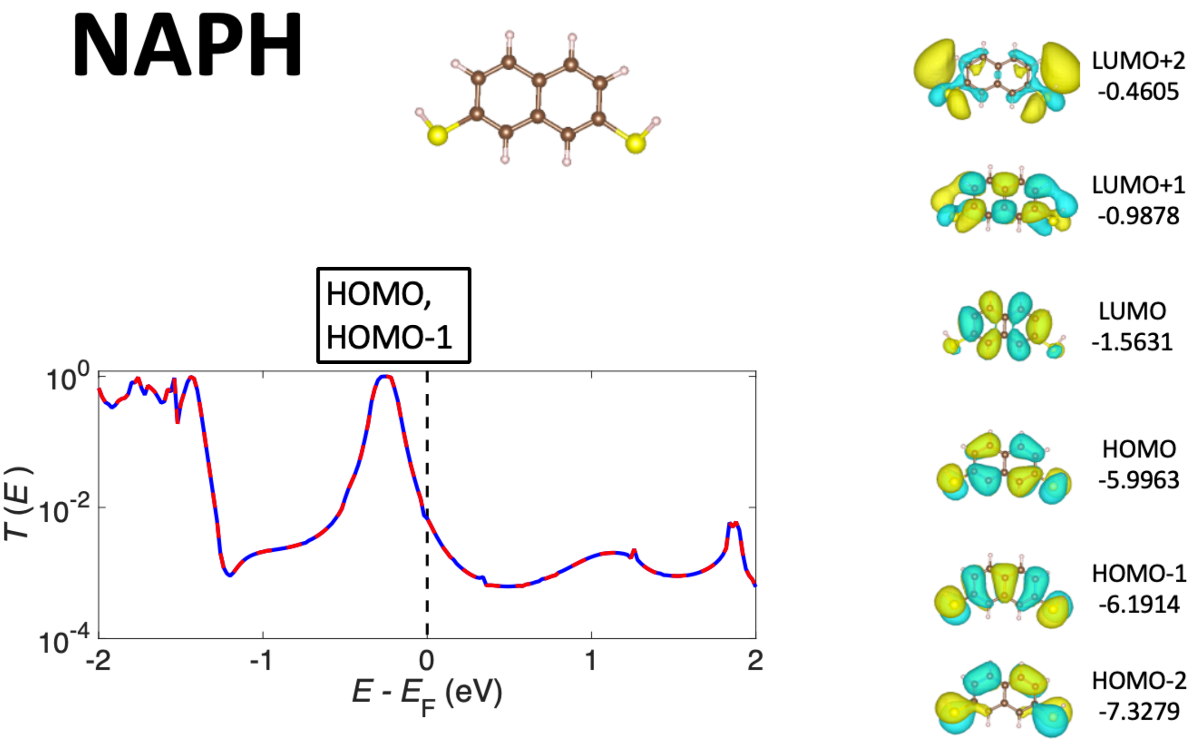

Figure S6: NAPH: MOs of isolated molecule with corresponding energies (eV) (right), and spin-resolved transmission spectra (α in blue, β in red) with assigned MOs responsible for transmission peaks (bottom left).

S3 Charge and Spin

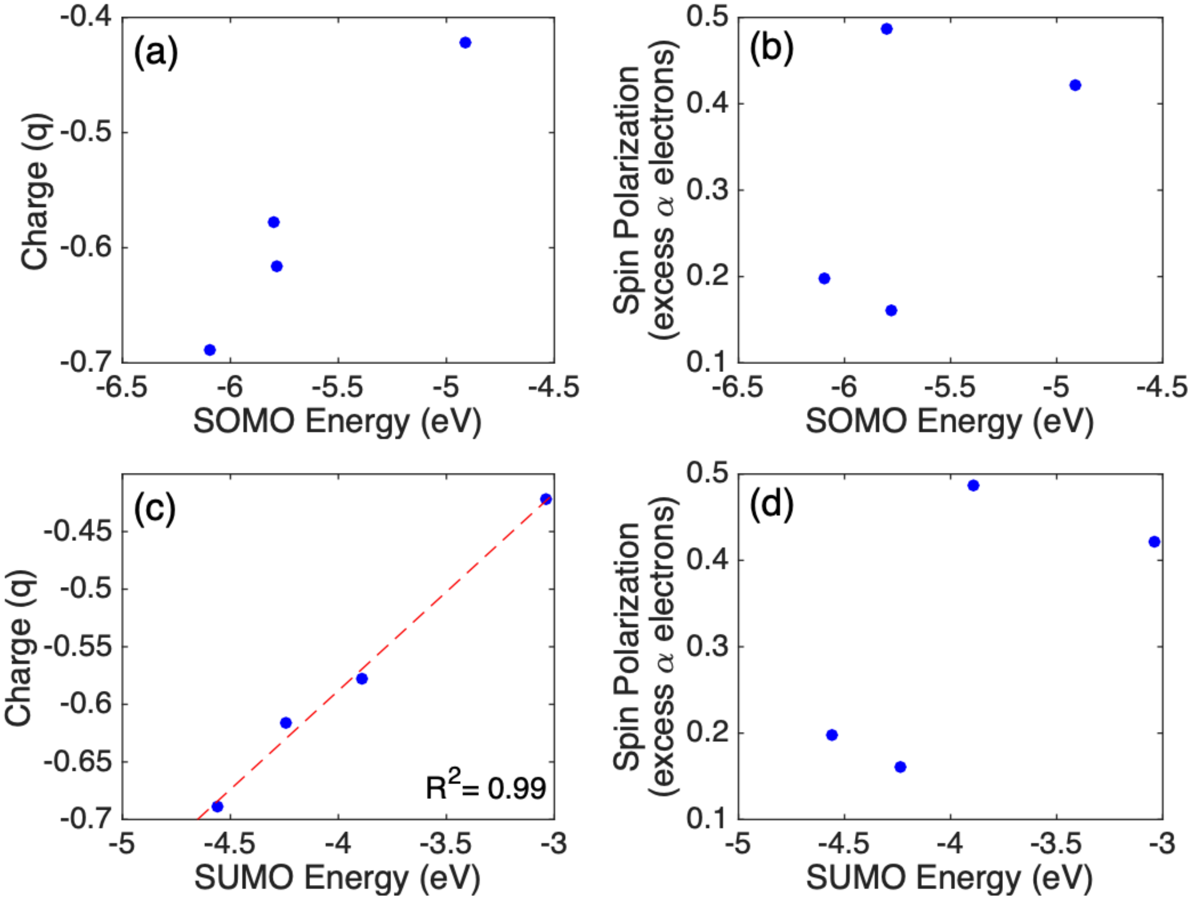

Figure S7: Relationships between charge (a,c) or zero-bias spin polarization (b,d) of the in-junction radical versus SOMO energy (a,b) or SUMO energy (c,d) of the isolated radical. There is an excellent correlation between charge and the SUMO energy.

S4 $I - V$ and SFE over larger bias window

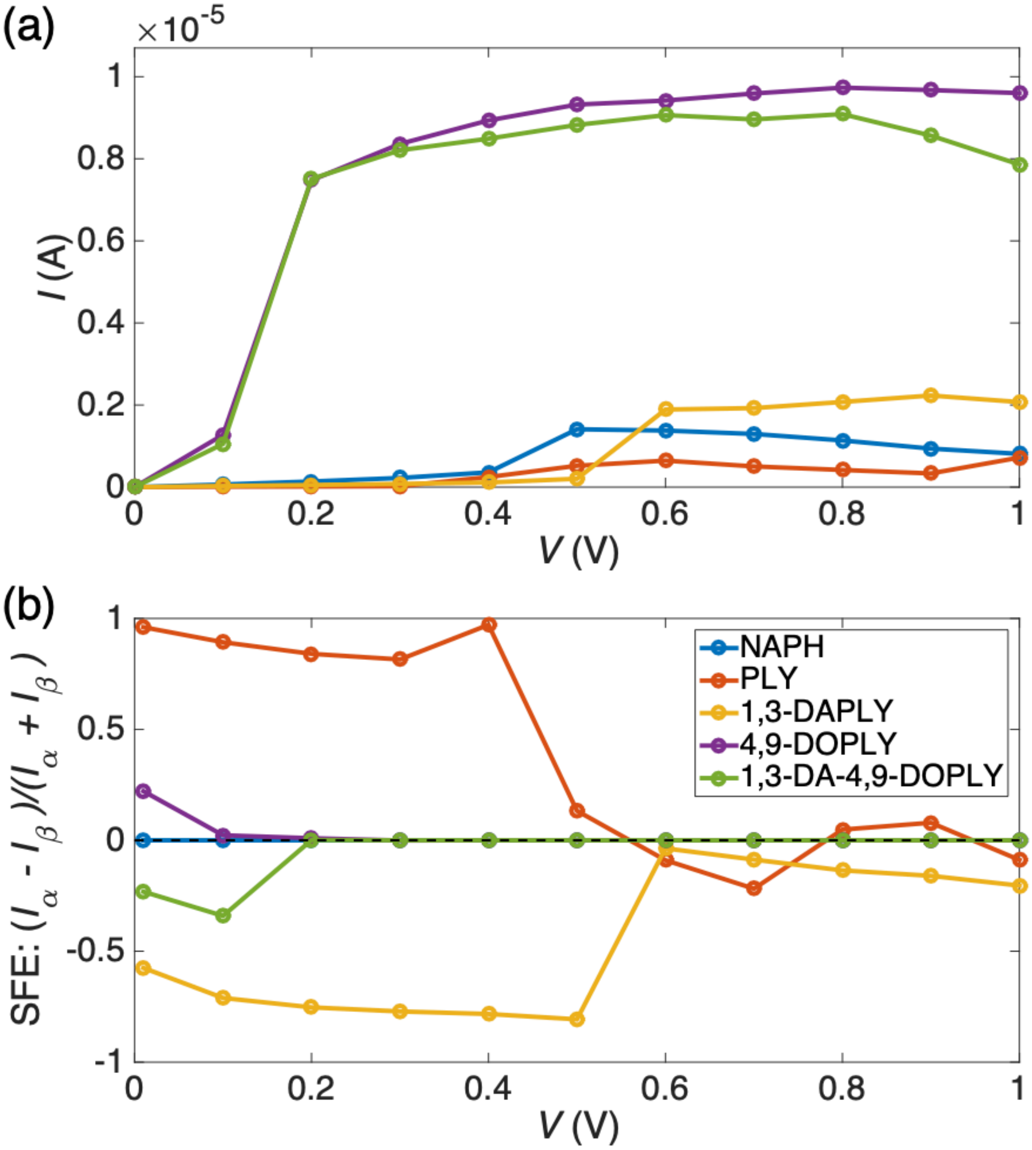

Figure S8: Bias-dependent current (a) and SFE (b) for naphthalene and the four PLY radicals up to 1.0 V.

References

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