

Supplementary information for

Dipole Effects on Formation of Molecular Junctions

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The Supplementary Information includes:

1. Supplementary Figures (Figs. S1-S3) and Tables (Tabs. S1 and S2).

1. Supplementary figures

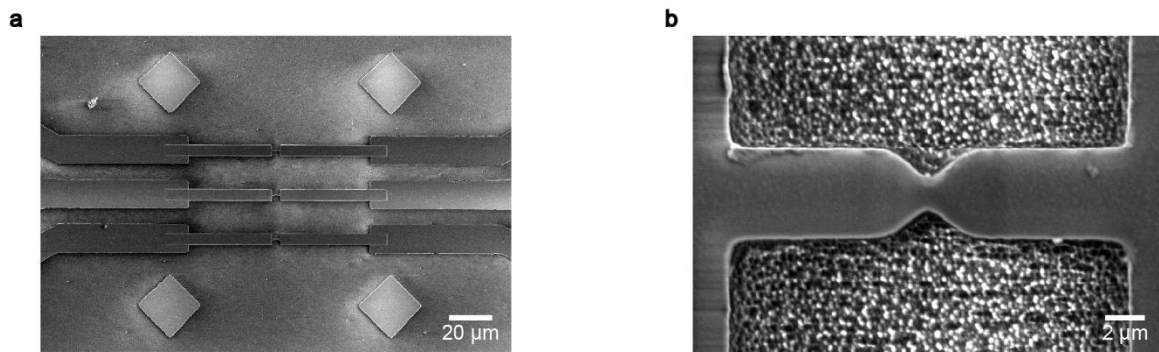


Figure S1. (a) Scanning electron micrographs of a SiO₂-coated MCBJ. (b) A magnified view showing 100 nm wide Au constriction.

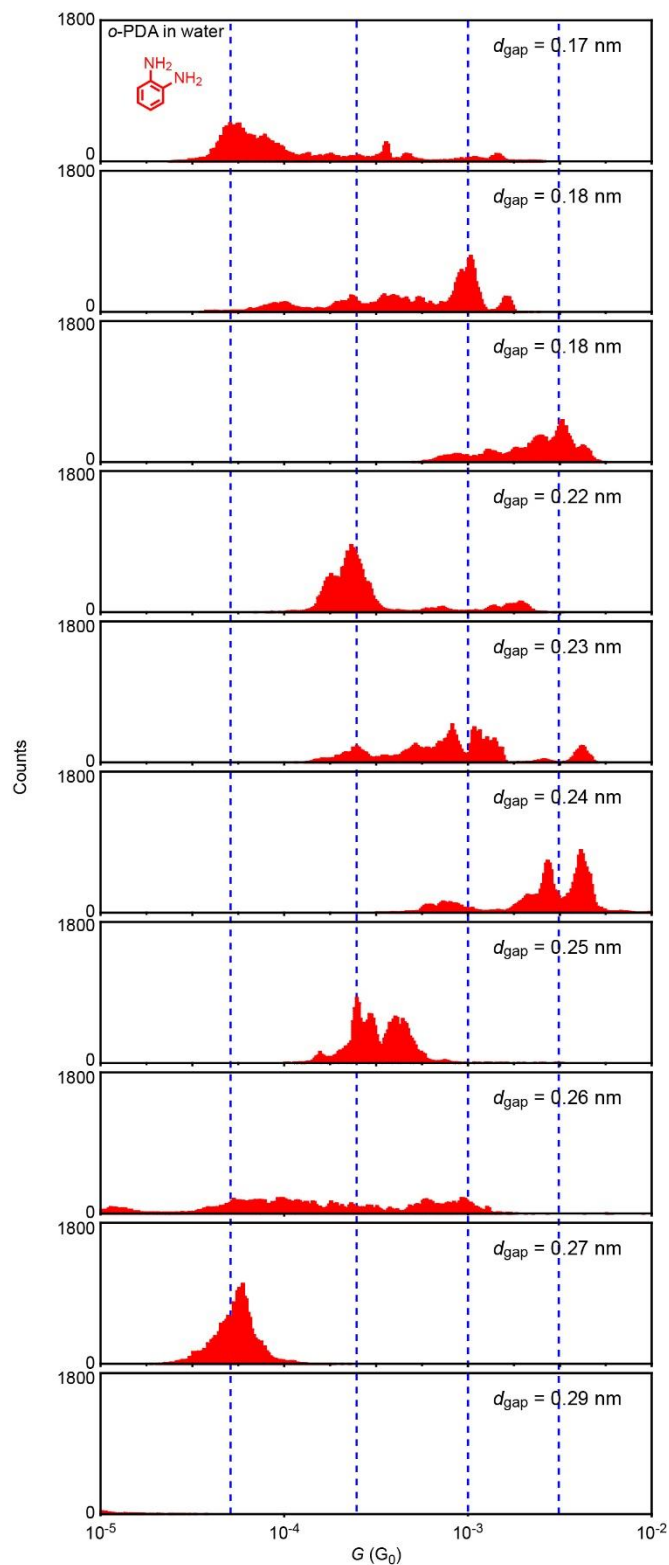


Figure S2. Separate conductance histograms constructed with the traces recorded in 1,2,4-trichlorobenzene solution of 1,2-benzenediamines using sub-molecular-sized electrode gaps. Broken lines denote the characteristic conductance states observed in Fig. 4 of the main text.

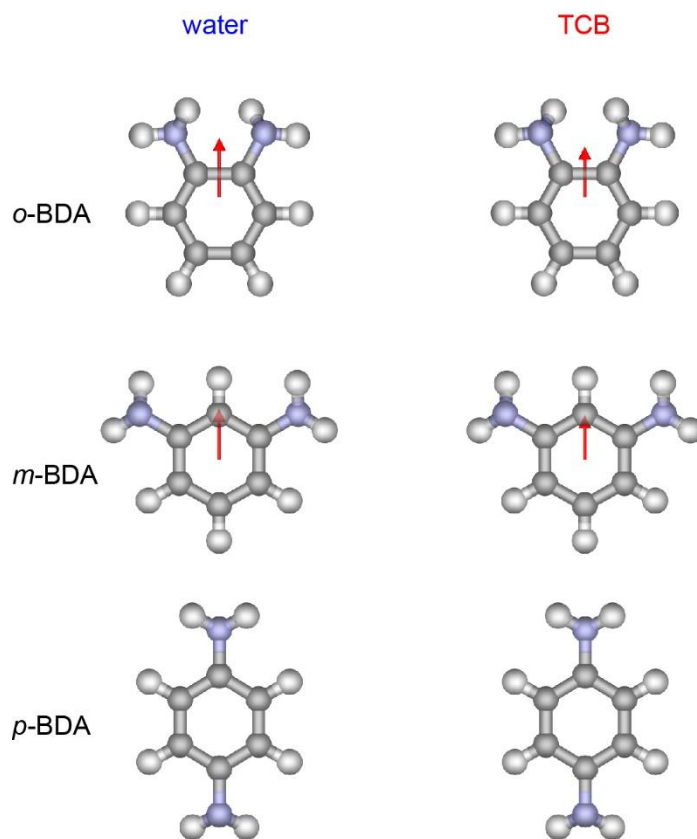
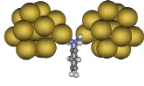
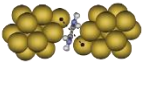
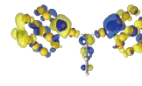
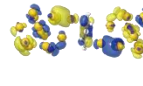
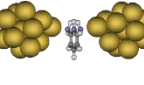
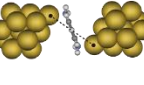
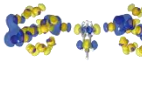
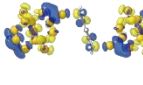
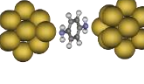
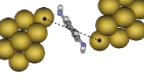
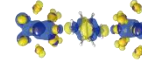
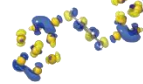


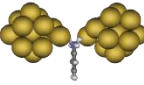
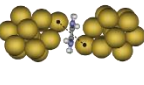
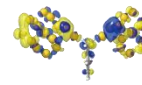
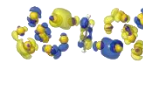
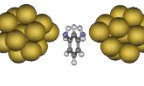
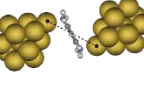
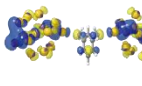
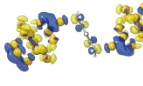
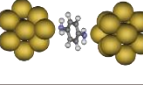
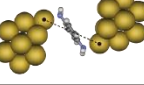
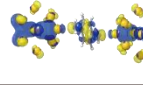
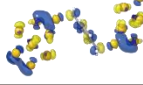
Figure S3. Dipole moments of BDA isomers in water (left) and 1,2,4-trichlorobenzene (TCB) (right). Arrows point the directions of the net dipole moments.

Table S1. Optimized structures and the frontier molecular orbital levels of benzenediamines (BDAs) in water. Dashed lines denote the distance between the center of Au atoms anchoring BDAs. The corresponding Au electrode distance includes the atomic radius of Au.

Molecular junction in water	Optimized Structure			Frontier molecular orbitals		
	Top View	Side View	Distance (nm)	Top View	Side View	HOMO -4 (eV)
Au ₁₄ - <i>o</i> -BDA-Au ₁₄			0.52 (0.23)			-5.18
Au ₁₄ - <i>m</i> -BDA-Au ₁₄			0.77 (0.48)			-5.25
Au ₁₄ - <i>p</i> -BDA-Au ₁₄			0.84 (0.55)			-5.19

* Values in parenthesis denote the distance after subtraction of Au atomic radius of 0.29 nm.

Table S2. Optimized structures and the frontier molecular orbital levels of benzenediamines (BDAs) in 1,2,4-trichlorobenzene (TCB). Dashed lines denote the distance between the center of Au atoms anchoring BDAs. The corresponding Au electrode distance includes the atomic radius of Au.

Molecular junction in TCB	Optimized Structure			Frontier molecular orbitals		
	Top View	Side View	Distance (nm)	Top View	Side View	HOMO-4 (eV)
Au ₁₄ - <i>o</i> -BDA-Au ₁₄			0.50 (0.21)			-5.39
Au ₁₄ - <i>m</i> -BDA-Au ₁₄			0.77 (0.48)			-5.46
Au ₁₄ - <i>p</i> -BDA-Au ₁₄			0.86 (0.57)			-5.37

* Values in parenthesis denote the distance after subtraction of Au atomic radius of 0.29 nm.