Electronic Supplementary Information

Raising the Barrier for Photoinduced DNA Charge Injection with a Cyclohexyl Artificial Base Pair

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Table 1: M/Z values for hairpins determined by MALDI-TOF mass spectrometry. Melting temperature of hairpins with/without cyclohexane. PDI samples were measured in water at pH 7.2 and rest of the samples was measured in 10 mM phosphate buffer with 100 mM NaCl.

| Sample ^a | m/z | | Tm (°C) | n C) | m/z | | |
|---------------------|------------|-------|------------|---------------------|------------|-------|------------|
| | calculated | found | | Sample ^a | calculated | found | Tm (°C) |
| SA-1 | 4084.66 | 4091 | 62 | NDI-3 | 4723.10 | 4730 | 54 |
| SA-2 | 4085.66 | 4092 | 67 | NDI-4 | 4724.10 | 4731 | 58 |
| SA-3 | 4722.98 | 4725 | 54 | NDI-SD-1 | 4446.88 | 4456 | 68 |
| SA-4 | 4723.98 | 4728 | 62 | NDI-SD-2 | 4450.88 | 4459 | 74 |
| PDI-1 | 4208.81 | 4214 | 52 | NDI-SD-3 | 5085.20 | 5095 | 58 |
| PDI-2 | 4209.81 | 4215 | 54 | NDI-SD-4 | 5089.20 | 5099 | 69 |
| PDI-3 | 4847.13 | 4852 | 48 | SA-SD-3 | 5085.08 | 5096 | 64 |
| PDI-4 | 4848.13 | 4853 | 55 | SA-SD-4 | 5089.08 | 5100 | 82 |
| NDI-1 | 4084.78 | 4090 | 64 | | | | |
| NDI-2 | 4085.78 | 4091 | 67 | | | | |

^aSee Chart 1 in main text for structures.



Figure S1. Circular dichroism spectra of hairpins and capped hairpins used in this study in phosphate buffer (10 mM phosphate, 0.1 M NaCl, pH 7.2, except for PDI hairpins).



Fig. S2 Transient absorption spectra of NDI diol in methanol.



Fig.S3 Transient absorption spectra of **SA–SD–3** and **SA–SD–4** in phosphate buffer (10 mM phosphate, 0.1 M NaCl, pH 7.2) at delay times from –1.0 ps to 6.6 ns.