Supporting Information

The capture of low-energy electrons by PNA versus DNA

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PNA Synthesis and Characterization

We have synthesized the PNA oligomers listed in Table S1. The PNA oligomers were purified by HPLC and characterized by MALDI-Tof (Table S1).

Table S1. Calculated masses of PNA oligomers and corresponding m/z observed from MALDI-ToF MS.(reflector mode, α-cyano-4-hydroxycinnamic acid matrix, laser intensity 1200-1800).

N→C Sequence of PNA oligomers	**Calculated m/z**	**Observed m/z**
N-end Thiol-EthylPNAs		
2ET-c4- TTTTTTTGTTTTTTT-**Lys_3**	4607.47	4607.70
2ET-c4- GTTGTTGTTGTTGTT-Lys_3	4707.15	4704.81
2ET-c4- **T**|**T**|**T**|**T**|**T**|**T**|**T**|**T**|**T**|**T**TTTT	4197.92	4211.65[a]
2ET-c4- TTTTTTTGTTTTTTT	4222.93	4220.01
2ET-c4- TTTTGTTTTGTTTTG	4272.96	4275.3
2ET-c4-GTTGTTGTTGTTGTT	4322.97	4321.45
C-end Thiol-EthylPNAs		
Lys_3-TTTTT|**T**TTTTT|**T**|**T**TT-c4-2ET	4554.59	4553.34[b]
Lys_3-TTTT|**T**T|**T**GTTT|**T**|**T**|**T**T-c4-2ET	4579.60	4575.95[c]
Lys_3-GTTTTG**TTTT**GTTTT -c4-2ET	4629.62	4622.70[d]
Lys_3-GTTGTTG|**T**TG|**T**|**T**GTT-c4-2ET	4679.64	4677.27[e]

[a] This PNA contained a small amount of shorter, capped PNA oligomers T_x, where x=4-14. None of the shorter PNAs contained the thiol-ethyl 2ET linker.

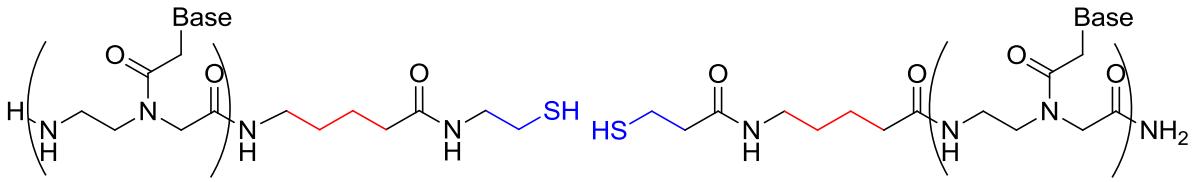
[b] This PNAcontaineda small amount of T_x-c4-2ET, where x=3,4,5 and 10.

[c] This PNA containeda small amount ofT_x-c4-2ET, where x=2-4, 2ET-c4-T_7GT and 2ET-c4-T_7GT_3.

[d] This PNA containeda small amount of T_xGT_4-c4-2ET, where x=1-4.

[e] This PNA containeda small amount of $T_2(GT_2)_2$-c4-2ET, T_2GT_2-c4-2ET, TGT_2-c4-2ET.

2ET stands for the ethyl-thiol linker used to anchor the PNA to the gold surface. This linker was introduced at either the N-end or C-end of the PNA (Scheme S1). A C4 spacer was introduced between 2ET and the PNA nucleobases (Figure S1).



(a) (b)

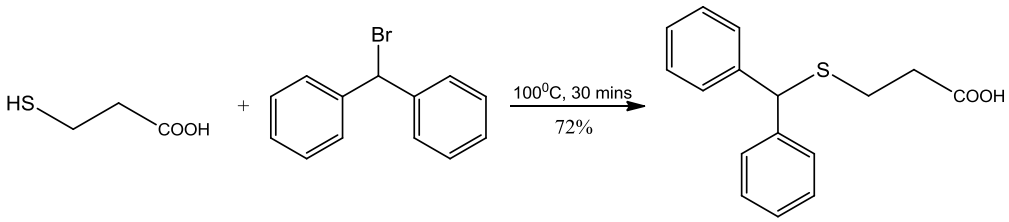
Figure S1. C-terminus (a) and N-terminus (b) thiol-modified PNA. The ethyl-thiol used to anchor the PNA to the Au surface is identified in blue. The C4 spacer is identified in red.

Solid-Phase PNA Synthesis. PNA monomers were purchased fromPolyOrg Inc. and used without further purification. 3-Benzhydryl-mercaptopropionic acid, which was necessary for the N-end modification of PNA with the thiol linker, was synthesized using a slightly modified published procedure (Scheme S1 and see below).[1]

The 5-aminovaleric acid, which was used to introduce a C4 linker between the ethyl-thiol end of the PNA and the first nucleobase, was purchased from Sigma Aldrich and was used as received. ThePNA oligomers with N-end ethyl thiolwere synthesized using the Boc strategy; the PNA

oligomers with C-end ethyl thiol were synthesized by Fmoc strategy.[2] A p-methyl-benzhydrylamineresin purchased from Peptide Internationalwas used for the Boc strategy. The2ET modification at C-end of PNAwas afforded by using cysteamine 2-chlorotrityl resin purchased from AnaSpec. The PNA was cleaved using TFMSA/TFA/m-cresol/thioanisole (20:60:10:10) and TFA/triisopropylsilane/water (95:2.5:2.5) for Boc and Fmoc strategy, respectively. The cleaved PNA was precipitated using ethyl ether and was purified byreverse-phase HPLC using a C_{18} silica column and a Waters 600 Controller and Pump. The absorbance was measured with a Waters 2996 Photodiode Array Detector. Characterization of the oligomers was performed by MALDI-ToF mass spectrometry on an Applied Biosystems Voyager Biospectrometry Workstation with Delayed Extraction, reflector mode and an α-cyano-4-hydroxycinnamic acid matrix (10 mg/mL in 1:1 water:acetonitrile, 0.1%TFA). The laser intensity is typically 1400 to 1900.

3-Benzhydrylmercaptopropionic acid. 3-Mercaptopropionic acid (0.47g, 4.5 mmol) was slowly added to bromodiphenylmethane (1.20 g, 4.8 mmol). After the initial reactionhad subsided, the mixture was heated to 100°C until there was no evolution of HBr (~30 minutes). The reaction mixture was then allowed to cool to room temperature and extracted with a saturated solution of NaHCO3. The aqueous layer was acidified with 1M HCl until a white solid precipitate appeared and then was placed on an ice bath for 30 minutes. The while precipitate was filtered and was recrystallized from aqueous ethanol yielding the productas a colorless solid (0.88 g, 72 %). ^{1}H NMR (300 MHz, CDCl3): δ = 7.44-7.20 (m, 10H, ArH), 5.22 (s, 1H, Ar2CH), 2.68 (m, 2H, CH2COOH) and 2.59 (m, 2H, CH2S).



Scheme S1. Synthesis of 3-Benzhydrylmercaptopropionic acid

Our first design of the PNA oligomers had the thiol-ethyl linker at the C-terminus (Figure S1a). In this synthesis of the C-end thiol-containing PNA, we could take advantage of the commercial availability of the cysteamine 2-chlorotrityl resin, which has the thiol-ethyl group on. The resin is compatible with Fmoc-protection synthetic strategy but not with Boc-protection strategy. However, in our experience the synthesis of long PNA oligomers by the Fmoc strategy gives lower yield than the synthesis by the Boc-protection strategy, which is possibly due to aggregation of the oligomer on the resin.[3] More specifically, during the PNA synthesis using the Fmoc strategy, once the PNA contained more than eight monomers, we frequently observed incomplete coupling and deprotection.The deprotection time was 60 minin 20% piperidine/DMF (v/v). Also, the mass spectrograms of crude samples of PNAs prepared using the Fmoc strategy showed truncated PNA sequences, which made purification of the PNA very challenging.

To make possible the synthesis of the PNAs by Boc-protection strategy, we decided to place the thiol-ethyl linker at the N-terminus of the PNA using the protected 3-mercaptopropionic acid and the p-methyl-benzhydrylamineresin (Figure S1b). Under these conditions, the synthesis of all PNA oligomers proceeded without difficulty**.** Nevertheless, the purification and characterization of T_{15}-C_4-**2ET** was challenging because the oligomer had low solubility in common solvents including water and acetonitrile.

Preparation of the Monolayers of PNA

Self-assembled monolayers of 3′-thiolated DNA 15-mers were prepared according to standard procedures[4,5] by incubating clean gold substrates[56] with a 20 □M solution of the ss DNA in pH 7.2 0.4 M potassium phosphate buffer. The clean Au slide was covered uniformly with the oligomer solution and kept overnight in a clean and controlled humid environment within a desiccator. Afterdeposition, the slides were washed thoroughly first withpH 7.2 0.4 M potassium phosphate buffer and subsequently with deionized water (Millipore). The samples were then dried in N_2.

Self-assembled monolayers of PNA were prepared similarly by incubating the clean gold substrates with 25 □M solutions of thethiol-modified PNAsin pH 7.2 10 mM potassium phosphate buffer. The clean Au slide covered uniformly with the oligomer solution was kept overnight in a clean and controlled humid environment.Afterdeposition, the slides were washed thoroughly first with the pH 7.2 10 mM potassium phosphate buffer and subsequently by deionized water (Millipore). The samples were then dried in N_2.

Characterizationof the Monolayers of PNA

DNA and PNA monolayers were characterized by FTIR (Figure S2) and XPS (Table S2). Based on both techniques, we conclude that the PNA monolayers were more densely packed than the DNA monolayers. The XPS results showed now free thiols, which indicates that the monolayers are densely packed and that there is no multilayer stacking. Additionally extensive rinsing of the PNA samples with 50% acetonitrile-water solution didn't showanysignificanteffect on the FTIR and LEPET spectra of the 2ET-modified PNA monolayers.

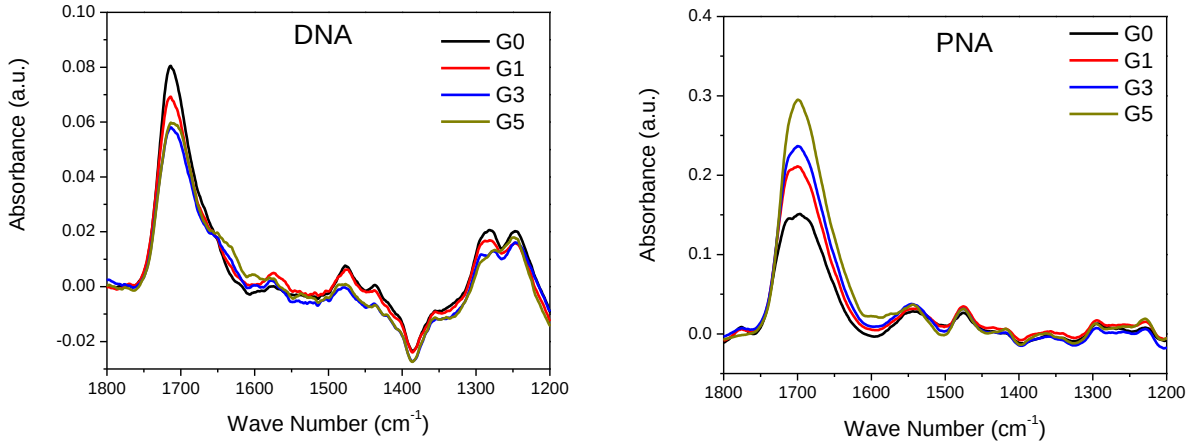


Figure S2. The FTIR spectra of DNA and PNA monolayers.Comparing the intensity of the absorbance peak the spectra suggests that the PNA monolayers are denser than the DNA monolayers.

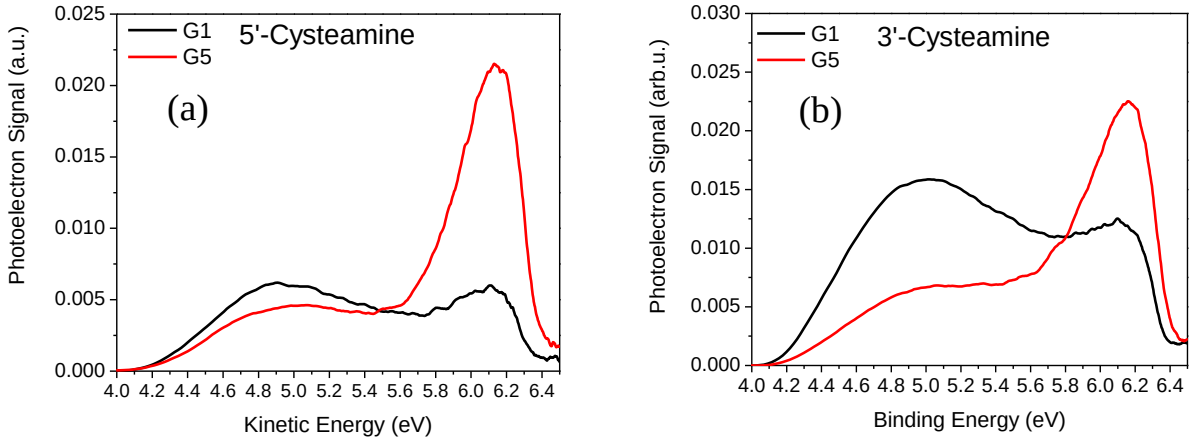


Figure S3. LEPET spectra of PNA SAMs attached to the surface through a thiol at the N (a) or C (b) terminus of the PNA.These spectra show that the effect of the guanine content on the photoelectron signal does not depend on the orientation of the PNA on the Au substrate.

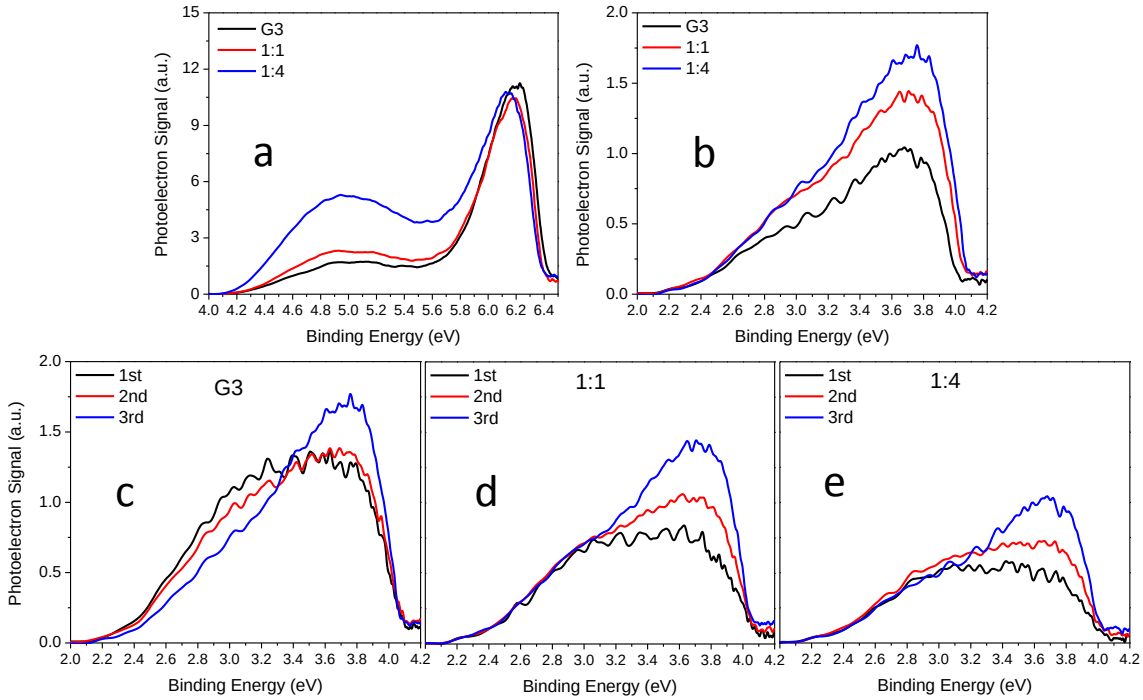


Figure S4. Mixtures of G0 and G3 PNA oligomers studied by LEPET (a) and TPPE (b). The intensity of the peaks decreases at low binding energy and increases at high binding energy as a function of time for G3:G0= 1:0, 1:1, 1:4 (c-e). This data suggests that the effect is molecular rather than cooperative.

Table S2. XPS results from PNA and DNA samples. The sulfur peaks in both DNA and PNA samples were almost entirely from reduced sulfur indicating that the sulfur in the SAMs made with 2ET-modified PNAs are attached to the Au substrate.

Atomic ratio	**C/N**		**C/O**		**O/N**		**N/P**	
Sample	PNA G5	DNA G5	PNA G5	DNA G5	PNA G5	DNA G5	PNA G5	DNA G5
Theoretical	2.26	3.4	3	1.53	0.74	2.22	N\A	3
Experimental (± 10%)	2.85	4.4	2.8	1.78	1.02	2.48	N\A	3.5

Fit of the TPPE spectrum to two peaks:

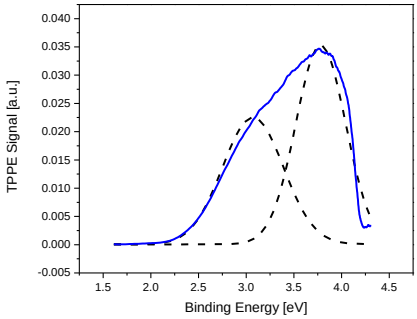


Fig. S5: The fit of the TPPE spectrum of PNA G3 to two peaks located at 3.0 and 3.8 eV.

References

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