1. Reagents and materials

1-Ethyl-3-(3’-dimethylaminopropyl)carbodiimide (EDC, water-soluble carbodiimide), N-hydroxysuccinimide (NHS) and glycogen (Type III, from rabbit liver) were purchased from Sigma-Aldrich (St. Louis, MO), 2-(N-morpholino)ethanesulfonic acid (MES) from Fluka (Buchs, CH), sodium chloride, tris(hydroxymethyl)aminomethane, sodium citrate, sodium dodecylsulfonate (SDS), and magnesium chloride from Caledon Laboratories Ltd (Georgetown, ON). All chemicals were of the highest available quality and used without further purification unless otherwise stated. All solutions were prepared with deionized water (>18.3 MΩ·cm) from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA). The 22-mer synthetic oligonucleotides used as probe/target strands in the experiments were of reverse-phase cartridge purification (RP1) grade and obtained from Sigma-Genosys (Oakville, ON).

Figure 1S. Optical photos of a regular CD-R (a) and its polycarbonate (PC) base (b).
Polycarbonate (PC) bases of compact discs (CDs) were provided by Millennium Compact Disc Industries Inc. (Vancouver, BC). They can also be prepared from regular CDs (or CD-Rs) by removing the reflective layer via scoring and vigorous rinsing with deionized water, removal of the dye layer with a rapid methanol rinse, 10 min ultrasonication in a 1:4 (v/v) methanol/water solution and a final rinse with deionized water. Photos of a normal CD-R and thus prepared PC base are shown in Figure 1S.

Transmittance electron microscopy (TEM) gold grids (G1000HSG, Pelco International) were used as masks for patterning the PC surfaces. They are made of 6-μm-diameter wires with a center-to-center spacing of 25 μm. The optical and scanning electron microscopy (SEM) images of this type of TEM grids are shown in Figure 2S.

![Figure 2S. Optical microscope image (left, 80×) and SEM image (right) of a TEM grid.](image)

2. Activation and patterning of the PC substrates by UV/ozone treatment

The photochemistry of polycarbonate exposed to UV light involves two photo-Fries reactions, a photo-induced oxidation of the side-chain and a benzene ring oxidation. The reaction pathway followed depends primarily on the excitation light source and the oxygen concentration. The main photochemical process occurring under irradiation at 254 nm in the presence of oxygen is the succession of two photo-Fries rearrangements leading to the formation of phenyl salicylate and dihydroxybenzophenone units. Competitively, some radicals react with oxygen to form hydroperoxides. Eventually the photo-oxidation leads to the formation of carboxylic acid groups.

The UV/ozone treatment of the PC surface was carried out with a UV/ozone system (Model PSD-UV, Novascan Technologies, Inc.). This apparatus uses a low-pressure mercury lamp, generating ultraviolet emission at both 185 nm (1.5 mW/cm²) and 254 nm (15 mW/cm²); the distance between the UV source and the PC sheet is 2.5 cm. In the presence of ambient oxygen, the
two-step photochemical process initiated by the photolysis of molecular oxygen at 185 nm produces a nominal steady–state concentration of highly reactive ozone which then decomposes by absorption of UV light at 254 nm.

3. Contact angle measurements of UV/ozone-treated PC surface

Contact angle measurement is one of the most convenient methods for the characterization of solid/liquid interfaces. Water contact angles on activated PC surfaces were measured with an AST Optima system at ambient conditions (22-26 °C, 43 ± 3% relative humidity) using a horizontal light beam to illuminate the liquid droplet. The contact angles measured here are equilibrated values of sessile liquid drops of either pure water or buffer solution.

The untreated sample is hydrophobic with a water contact angle of 88 ± 2°. During UV/ozone treatment, the surface became more and more hydrophilic (Figure 1 in the main text) with increasing irradiation time. After 10 min, the angle remained constant at 20 ± 2°. In contrast, the water contact angles decreased to a similar value after at least 15 hours when the PC substrates were irradiated with normal UV light at 254 nm (Photoreactor LZC-4V, Luzchem Research, Inc.). The same trend was observed when the PC substrates were micro-patterned with TEM grids as masks during the UV/ozone treatment.

For the contact angle titration (Figure 3 in the main text), the activated PC samples were immersed in the buffer solution for 30 s before the contact angle was measured. The buffer solutions were prepared according to Creager et al. as follows: pH 0-1, perchloric acid; pH 2-3, phosphoric acid/sodium phosphate monobasic; pH 4-5, acetic acid/sodium acetate; pH 6-8, sodium phosphate monobasic/sodium phosphate dibasic; pH 9-11, sodium bicarbonate/sodium carbonate; pH 12, sodium phosphate dibasic/sodium phosphate tribasic. In all cases, the ionic strength was kept constant (0.01 M). The exact pH values for the buffer solutions were recorded before and after the contact angle measurements. The contact angle transition between pH 4 and 9 corresponds to the ionization of surface carboxylic acid groups. As these groups are transformed to carboxylate groups upon exposure to a basic aqueous buffer solution, the surface becomes more hydrophilic: the free energy of the solid/liquid interface becomes lower and the contact angle decreases. The process of surface ionization is fully reversible as indicated by reproducible contact angle measurements.

4. Determination of the surface density of carboxylic acid groups on activated PC

To determine the surface density of carboxylic acid groups (COOH) groups resulting from UV/ozone treatment, a cationic dye, crystal violet (Scheme IS), was used. This method relies on the
electrostatic interactions between crystal violet molecules and carboxylate groups. First, the UV/ozone-irradiated substrates were covered with a crystal violet solution (1 mM) for 5 min. After rinsing with water, the samples were incubated first with ethanol (80 % v/v) and second with 0.10 M HCl (in 20% ethanol) until the dye could no longer be observed on the sample surface. Then the solutions from the two incubations were combined and absorbance readings were taken with a UV/Vis spectrometer. The concentration of crystal violet released from the surface was calculated from Beer’s law (\(A = εc\)) and used to determine the surface density of COOH groups. The value reported in the main text (\(4.8 ± 0.2 \times 10^{-10} \text{ mol/cm}^2\)) is an average over three samples.

5. XPS confirmation of the carboxylic acid groups generated on PC upon UV/ozone treatment

The generation of reactive carboxylic acid groups was further confirmed by x-ray photoelectron spectroscopic (XPS) studies of three types of PC samples: original, UV/ozone-

![Figure 3S](image_url)

**Figure 3S.** X-ray photoelectron C 1s and O 1s signals of the PC substrate before (●) and after UV/ozone treatment (▼) and irradiation through a TEM grid (○) for 10 min.

treated, and UV/ozone-irradiated through a TEM grid. The characteristic C 1s and O 1s signals are shown in Figure 3S. The C 1s spectrum of untreated substrate consists of two main components with binding energies of 284.6 eV and 291.0 eV, respectively, which are arising from the aryl or
alkyl carbons, and from the carbonate units (-OCOO-). The appearance of a distinct shoulder peak at high binding energy (288.6 eV) on sample exposure to UV/ozone indicates the generation of carboxylic acid groups (-COOH). The patterned surface showed less significant changes upon UV/ozone treatment, and the intensity of the C 1s signal at 284.6 eV decreased gradually. The O 1s peak of the untreated PC substrate showed both O=C and O−C components with binding energies of 532.3 and 534.0 eV, respectively, whereas irradiated substrates exhibited a broad peak centered at 533.0 eV, which is resulting from the new species.

6. Comparison of the surface activation efficiency by different UV irradiation methods

As shown in Table S1, the surface density of active groups (and the surface wettability) on polymeric materials upon UV treatment depends on the exact irradiation conditions (such as wavelength, powder, and duration). Compared with other UV irradiation methods, the UV/ozone protocol described in this paper shows higher surface activation efficiency, especially for PC substrates, i.e., shorter reaction time and higher –COOH surface density.

Table S1. Comparison of surface activation efficiencies of different UV irradiation methods

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>UV irradiation condition (wavelength, power and distance from the light source)</th>
<th>Surface wettability (before/after) and the irradiation duration</th>
<th>Active groups surface density / (10^{10})mol cm(^{-2}) and time dependence</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>240–425 nm, 15 mW cm(^{-2}) (maximum), d = 1 cm</td>
<td>70° / 24°(30 min)</td>
<td>(\Gamma_{\text{COOH}} = 13.12 \pm 0.93) (30 min)</td>
<td>13</td>
</tr>
<tr>
<td>PMMA</td>
<td>254 nm, 15 mW cm(^{-2}), d = 1 cm</td>
<td></td>
<td>(\Gamma_{\text{DNA probe}} = 0.41) (PMMA, 15 min)</td>
<td>14</td>
</tr>
<tr>
<td>PMMA, PC</td>
<td>254 nm, 15 mW cm(^{-2}), d = 1 cm</td>
<td>70° / 52°(PMMA, 2 h) 83° / 50°(PC, 2 h)</td>
<td>(\Gamma_{\text{COOH}} = 10) (PMMA, 20 min) 1.0 (PC, 20 min)</td>
<td>15</td>
</tr>
<tr>
<td>PS, PC</td>
<td>185 nm, 15 W, d = 10 cm</td>
<td></td>
<td>(\Gamma_{\text{peroxide}} = 20) (PS, 20 min) 5.0 (PC, 20 min)</td>
<td>16</td>
</tr>
<tr>
<td>PMMA</td>
<td>*Vacuum Ultraviolet 172 nm, 10 mW cm(^{-2}), d = 2 cm</td>
<td>80° / 30°(10(^{3}) Pa, 30 min)</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>PC</td>
<td>220 nm, 4W</td>
<td>70° / 20°(6.5 h)</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>PC</td>
<td>185 nm (1.5 mW cm(^{-2})) + 254 nm (15 mW cm(^{-2})) + ozone, d = 2.5 cm</td>
<td>88° / 20°(10 min)</td>
<td>(\Gamma_{\text{COOH}} = 4.8 \pm 0.2) (10 min) (\Gamma_{\text{DNA probe}} = 0.054 \pm 0.003)</td>
<td>This work</td>
</tr>
</tbody>
</table>

PMMA (polymethylmethacrylate), PS (polystyrene), PC (polycarbonate)

7. Photo-patternning of PC and passive DNA immobilization/hybridization

Scheme IIS shows the three steps of the experiment: surface activation/patterning, attachment of DNA probe strands, and hybridization/detection of the target strands. The transparent CD bases were cut into small pieces (2 \(\times\) 4 cm\(^2\)), placed into the UV/ozone chamber and irradiated
for 10 min through a TEM grid. Upon completion, they were left in the ozone environment for 25 min. After the activation step, 10 μL of a 10 μM solution of DNA probe strands in 0.1 M MES buffer at pH 6.5 (also containing 5 mM EDC and 0.33 mM NHS) were spread onto the patterned PC surface, and the sample was incubated for 2 hours under ambient conditions. The PC substrate modified with DNA probe strands was then washed with 0.01 M MES buffer and blow-dried with N₂ gas. To passivate unreacted carboxylic acid groups, the surface was washed with a dilute solution of glycogen (1 mg/mL) prior to hybridization. A 10 μM solution (10 μL) of fluorescein-labeled DNA target strands (0.1 M MgCl₂ and 1 M NaCl in 10 mM Tris-HCl buffer) was then spread onto the surface. The hybridization was facilitated by heating to 90 ºC, then cooling slowly to room temperature.¹⁹

After hybridization the PC chips were imaged on a Zeiss LSM 410 (Oberkochen, Germany) confocal microscope equipped with a ×25 (NA 0.8) multi-immersion objective. An argon/krypton mixed gas laser with excitation lines at 488, 568, and 647 nm was used to induce fluorescence. Excitation of the green fluorophore was achieved at 488 nm (the effective excitation range of 488-495 nm for fluorescein closely matches the photo-emission of an argon laser), and the resulting fluorescence was observed by using a 515–540 nm band pass filter.

8. Creation of DNA microarrays with microfluidic channel plates

A small PDMS plate with 8 to 12 microchannels (300 μm wide and 25 μm deep) was laid on top of an activated PC substrate; Figure 4S shows the optical image of PDMS plates placed on a CD base. The probe solution (0.5 μL) containing 5'-amine-modified DNA molecules (10-50 μM in phosphate buffer, 0.10 M, pH 7.0) was injected into the reservoir on one terminal of a microchannel and passed through the channel by suction from the other end. After 10 hours incubation in a humid box at room temperature, the channel was washed with the phosphate buffer.
The PDMS plate was then peeled off from the PC substrate. The surface was “blocked” with glycogen and washed again with the phosphate buffer. Another PDMS plate was then laid on top of the polycarbonate chip, but in a perpendicular orientation with respect the first plate. Hybridization with Cy5-labeled DNA samples (1-2 µM) in pH 7.4 buffer (10 mM Tris, 500 mM NaCl, 50 mM MgCl₂) or in × 1 SSC pH 7.0 buffer (15 mM Na₂C₂O₄, 150 mM NaCl, 0.15% SDS) was carried out at 20-40 °C for 30-60 min.

After hybridization, the microchip was washed sequentially with three buffers (pH 7.4): Tris (10 mM) + NaCl (50 mM), Tris (10 mM) + NaCl (10 mM), and Tris (10 mM) only. If an SSC buffer was used in the hybridization experiment, it was also used to wash the microchip twice. Afterwards, the PC chip was rinsed with water and dried with nitrogen gas. A confocal laser-fluorescent scanner (Typhoon 9410, Amersham Biosystems) at a resolution of 25 µm was used to examine the efficiency of marker strand immobilization and of the hybridization. In Figures 5S-8S, additional experimental results, including reproducibility tests and temperature/target concentration dependence in the hybridization tests are presented.
**Figure 5S.** Distribution of the fluorescence intensity in a $7 \times 7$ array resulting from the hybridization of *Probe I* and *Target II*; these data are corresponding to those of Figure 8(b) in the main text.

**Figure 6S.** Comparison of the fluorescence intensities and spot sizes upon hybridization of *Probe I* and *Target II* on two different chips prepared under identical conditions.
Figure 7S. Fluorescence image resulting from the hybridization of complementary probe (Probe I) and target (Target II) at varying target concentrations.

Figure 8S. The effect of incubation time (a) and washing temperature (b) on the signal discrimination ratio between single-base pair mismatch (Probe II-Target II) and perfect-match hybridization (Probe I-Target II) experiments.
References:


(10) Adamson, A. W. *Physical Chemistry of Surfaces*, Wiley: New York, **1982**.


