Supporting Information

A chemosensor for selective determination of 2,4,6-trinitrophenol using a custom designed imprinted polymer recognition unit cross-linked to a fluorophore transducer

Tan-Phat Huynh, Agnieszka Wojnarowicz, Anna Kelm, Piotr Woznicki, Pawel Borowicz, Alina Majka, Francis D’Souza and Wlodzimierz Kutner

a Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland
b Department of Chemistry, University of North Texas, Denton, 1155, Union Circle, #305070 TX76203-5017, USA
c Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszynski University in Warsaw, Woycickiego 1/3, 01-938 Warsaw, Poland
1 These authors equally contributed to this work.

*Corresponding author. Email address: thuyhk@ichf.edu.pl; wkutner@ichf.edu.pl; francis.douza@unt.edu
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Appendix 1S. Experimental

Chemicals and materials

2,4,6-Trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), phenol, acetonitrile, toluene, and tetra-
n-butylammonium perchlorate [(TBA)ClO₄] were purchased from Sigma-Aldrich. CLM₁,² and NH₂-S₄³ were prepared according to known procedures.

The 10-Ω/cm² indium-tin oxide (ITO) coated glass slides were supplied by Delta Technologies.

Instrumentation and procedures

The UV-vis spectra were recorded with 0.1-nm resolution using an UV-2550 spectrophotometer of Shimadzu, controlled by the UVProbe 2.21 software of the same manufacturer.

The potentiodynamic, differential pulse voltammetric, and electrochemical impedance spectroscopic measurements were performed at the ITO-coated glass slides, or 1-mm diameter Pt disk electrode using an AUTOLAB computerized electrochemistry system of Eco Chemie equipped with expansion cards of the PGSTAT 12 potentiostat and the FRA2 frequency response analyzer, and controlled by the GPES 4.9 software of the same manufacturer.

The polymer films were imaged by atomic force microscopy (AFM) using a MultiMode® 8 AFM microscope under control of a Nanoscope V controller of Bruker. A mode utilized for sample imaging was the Tapping Mode. For that, the RFESP probes of Bruker were used. The films for imaging were deposited on the ITO-coated glass slides.

The infrared (IR) spectra were recorded with a Vertex 80v Fourier transform infrared (FTIR) spectrophotometer equipped with the DLaTGS detector of Bruker. The polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS) spectra of the TNP drop-cast film and the MIP film were recorded using a Vertex 80v FTIR spectrophotometer with the PMA50 module equipped with a nitrogen-cooled MCT (Hg-Cd-Te) detector. To record these spectra, polymer films were deposited on the 0.3-cm² ITO-film coated glass slides. All IR spectra were analyzed with the OPUS 6.5 software of Bruker.

The theoretical IR spectra were generated within harmonic approximation using the Density Functional Theory method at the B3LYP approximation using the 6-31G basis-set included in the Gaussian 09 software package.⁴ To assign vibrations to bands in the spectra
measured, a two-step procedure was applied. The Vibrational Energy Distribution Analysis (VEDA) used was the first step of this procedure. In this step, the calculated IR spectra (so called normal modes) were described in terms of vibrations of internal coordinates (so called local modes). This assignment was accomplished with the VEDA software, in detail described in literature. In the second step, the latter modes were scaled with the SPESCA software in order to compare the experimental IR spectra with the calculated vibrational spectra. This software uses weighted linear regression in order to fit theoretical frequencies to experimental bands.

The fluorescence spectra were recorded with a model FL3-22 of Fluorolog-3 spectrofluorometer of Horiba Jobin Yvon. The emission spectra of the MIP films were recorded by mounting the ITO glass slides coated with the MIP films in the J1933 solid sample holder at 30° with respect to the excitation light beam. For analytical measurements, the MIP-TNP film was wetted with a drop (~20 µL) of the analyte or interference acetonitrile solution. After solvent evaporation, fluorescence spectra of polymer films were recorded at the 350-nm excitation wavelength.

The fluorescence quantum yield measurement was carried out using the Quanta-φ integrating sphere attached to the Fluorolog-3 spectrofluorometer. Prior to the measurement, the MIP-TNP film was dissolved in THF and drop-cast onto a microscope quartz cover slide. The procedures used herein were adopted from literature where details can be found.

Fabrication of the MIP-TNP and NIP films

Before deposition of MIP films, the ITO-coated glass slides were rinsed with toluene. Next, they were cleaned with acetone for 20 min, then with water for 20 min, and finally with isopropanol for 10 min.

Deposition of the MIP-TNP films on the ITO-coated glass slide working electrode involved potentiodynamic electropolymerization of the pre-polymerization complex of TNP with NH2-S4 in the potential range of 0.50 to 1.25 V vs. Ag/AgCl at the scan rate of 20 mV/s. An ITO-coated glass slide was used as the counter electrode in a parallel arrangement with the working electrode with a gap of ~2 mm. The growth of the MIP-TNP films was controlled with the number of potential cycles. After electropolymerization, the MIP-TNP films were rinsed with the abundant acetonitrile in order to remove excess of the supporting electrolyte solution.
Then, the TNP template was extracted from the MIP film with methanol for 4 h at room temperature under magnetic stirring conditions.\(^3\)

The same procedure was used to deposit a control non-imprinted polymer (NIP) film, except for the absence of the TNP template in the solution for the electropolymerization.


Scheme 1S. A proposed simplified structural formula of the pre-polymerization complex of TNP with the polymerized MIP.
Figure 1S. The normalized (1) absorption and (2) emission spectrum of the CLM in toluene for excitation at 375 nm.
Figure 2S. (a) Steady-state fluorescence spectra of CLM quenched by the TNP titrant in toluene; excitation at 350 nm. Concentration of CLM was 0.25 mM and that of TNP ranged from 0.05 to 0.38 mM. (b) Plot of quenching of fluorescence intensity with the change of the TNP concentration.
Figure 3S. (a) The potentiodynamic curve recorded at the ITO-coated glass slide for the 0.6 mM CLM, 0.1 M (TBA)ClO₄ solution of the acetonitrile-to-toluene volume ratio of 95 : 5. The potential scan rate was 20 mV/s. (b) The normalized emission spectrum for excitation at 350 nm of the CLM polymer film deposited on the ITO glass slide by potentiodynamic electropolymerization.
Figure 4S. The PM-IRRAS spectra for the ITO glass slides coated with (a) the TNP drop-cast film and (b) the TNP-templated MIP-TNP film deposited by potentiodynamic electropolymerization; conditions of this electropolymerization are described in caption to Figure S1a. Assignment of *ab-initio* calculated normal modes is represented by vertical arrows: (solid) –NC stretching, (dash) –NO stretching.