Supporting information

Label-Free Creatinine Optical Sensing Using Molecularly Imprinted Titanium Dioxide-Polycarboxylic Acid Hybrid Thin Films: A Preliminary Study for Urine Sample Analysis

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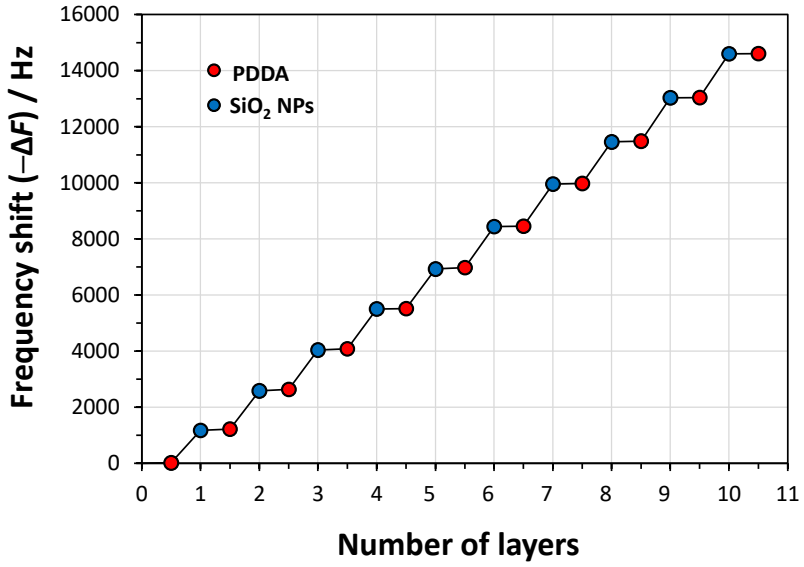

Figure S1. 9-MHz QCM frequency shifts measured during the same LbL electrostatic self-assembly of PDDA and SiO_2 NPs, showing an average frequency shift of 28 ± 17 Hz and 1430 ± 115 Hz per cycle of PDDA and SiO_2 NPs, respectively.

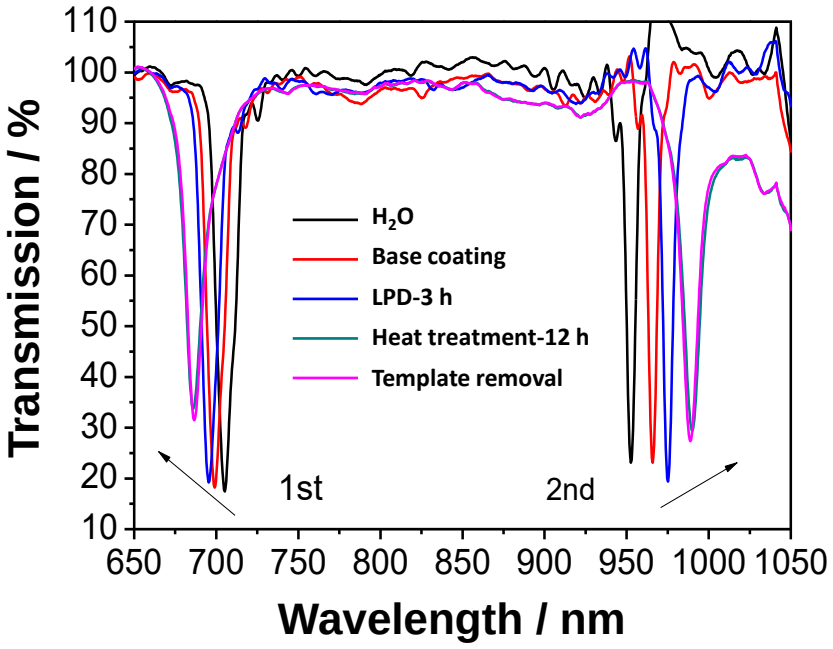

Figure S2. Changes in the TS of the LPG with a base coating measured in water before and after deposition of the PAA/TiO_2 (1 mM PAA) film for 3 h, after heat treatment at 60°C for 12 h, and after template removal.

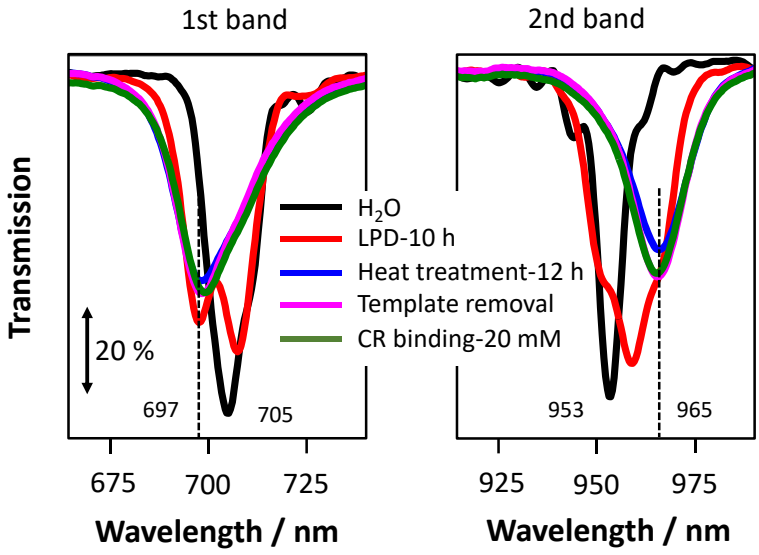

Figure S3. Changes in the TS of the LPG coated without a base coating measured in water before and after deposition of the CR@PAA/TiO_2 (2 mM CR and 6 mM PAA) film for 10 h, after heat treatment at 60°C (humidity 90%) for 12 h, and after template removal by HCl washing, subsequently followed by CR rebinding using a solution of 20 mM CR at 6.8 pH.

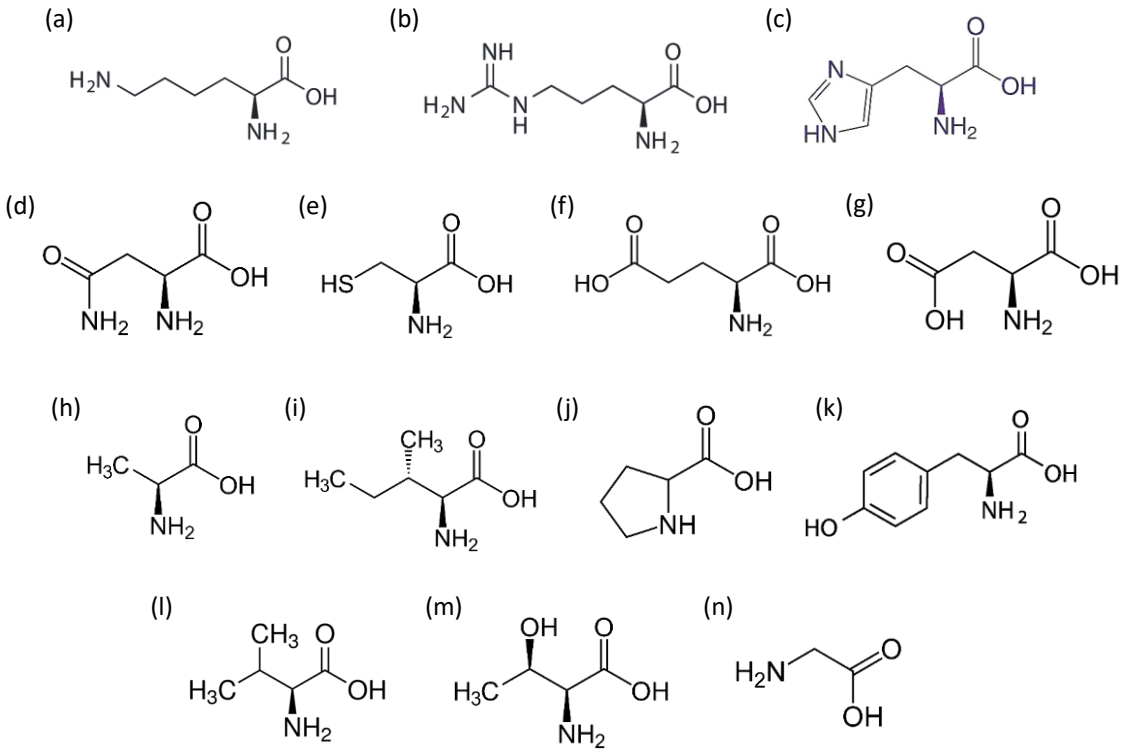

Figure S4. Chemical structures of amino acid guest molecules used in this study: (a) lysine, (b) arginine, (c) histidine, (d) asparagine, (e) cysteine (f) glutamic acid, (g) aspartic acid, (h) alanine, (i) isoleucine, (j) proline, (k) tyrosine, (l) valine, (m) threonine, and (n) glycine.

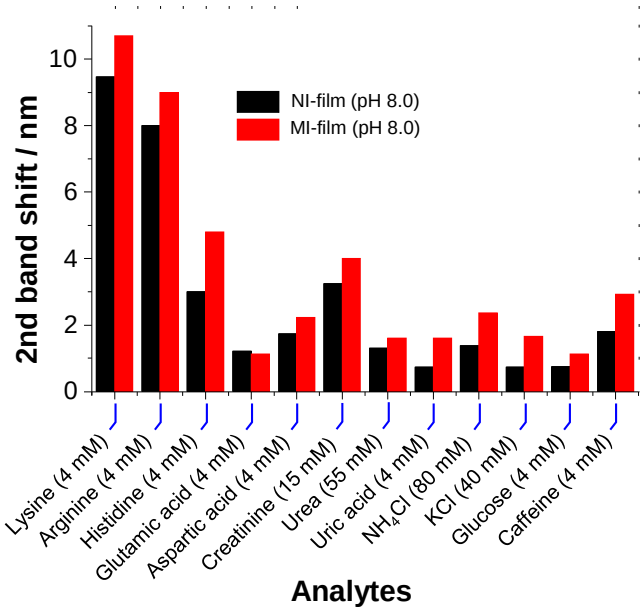

Figure S5. Comparison of the wavelength shifts of the second LPD band upon exposure of the NI and MI films to the CR and guest molecules at pH 8.0.

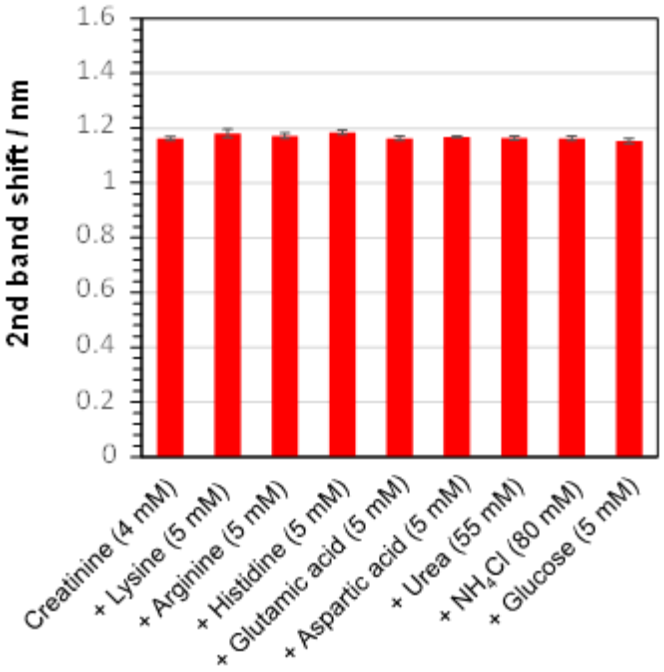

Figure S6. Comparison of the wavelength shifts ($n = 3$) of the second LPG band upon exposure of the MI film to CR (4 mM) or a binary mixture including CR (4 mM) at pH 6.8.

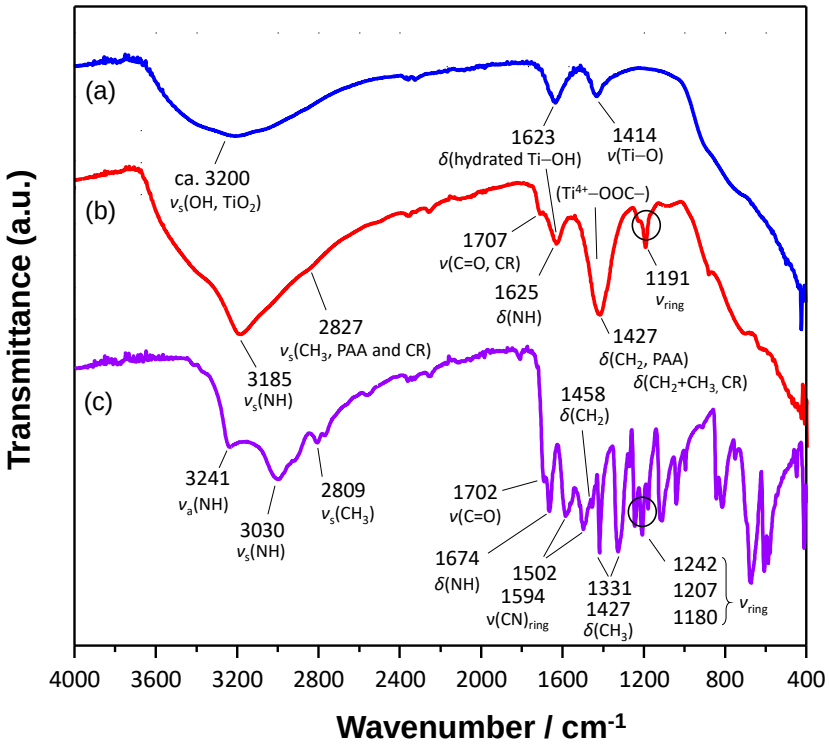

Figure S7. ATR-FTIR spectra of the solid samples of (a) pure TiO_2, (b) CR@PAA/TiO_2, and (c) pristine CR.

Table S1. Molecular properties of guest molecules including amino acids used in this study [1].

Compound	Molecular weight (g mol^{-1})	Molecular formula	Expressive formula	pK_{a1}	pK_{a2}	N [a]
Lysine	146.19	$C_6H_{14}N_2O_2$	H_2N-$(CH_2)_4$-CH(NH_2)-COOH	2.74	10.3	2
Arginine	174.20	$C_6H_{14}N_4O_2$	HN=C(NH_2)-NH-$(CH_2)_3$-CH(NH_2)-COOH	2.41	12.4	4
Histidine	155.15	$C_6H_9N_3O_2$	NH-CH=N-CH=C-CH_2-CH(NH_2)-COOH	1.85	9.44	3
Asparagine	132.12	$C_4H_7NO_4$	H_2N(O)C-CH_2-CH(NH_2)-COOH	2.00	8.43	1
Creatinine	113.12	$C_4H_7N_3O$	Hetero cyclic	4.96	9.21	3
Cysteine	121.16	$C_3H_7NO_2S$	HS-CH_2-CH(NH_2)-COOH	2.35	9.05	1
Glutamic acid	147.13	$C_5H_9NO_4$	HOOC-$(CH_2)_2$-CH(NH_2)-COOH	1.88	9.54	1
Aspartic acid	133.11	$C_4H_7NO_4$	HOOCCH_2CH(COOH)NH_2	1.99	9.90	1
Alanine	89.09	$C_3H_7NO_2$	CH_3-CH(NH_2)-COOH	2.47	9.48	1
Isoleucine	131.17	$C_6H_{13}NO_2$	CH_3-CH_2-CH(CH_3)-CH(NH_2)-COOH	2.79	9.59	1
Proline	115.13	$C_5H_9NO_2$	NH-$(CH_2)_3$-CH-COOH	1.94	11.3	1
Tyrosine	181.19	$C_9H_{11}NO_3$	HO-Ph-CH_2-CH(NH_2)-COOH	2.00	9.19	1
Valine	117.15	$C_5H_{11}NO_2$	$(CH_3)_2$-CH-CH(NH_2)-COOH	2.72	9.60	1
Threonine	119.12	$C_4H_9NO_3$	CH_3-CH(OH)-CH(NH_2)-COOH	2.21	9.00	1
Glycine	75.07	$C_2H_5NO_2$	NH_2-CH_2-COOH	2.31	9.24	1
Glucose	180.16	$C_6H_{12}O_6$	Cyclic			0
Urea	60.06	CH_4N_2O	H_2N(O)C-NH_2			2
Uric acid	168.11	$C_5H_4N_4O_3$	Hetero cyclic			
Caffeine	194.19	$C_8H_{10}N_4O_2$	Hetero cyclic			

[a] Number of nitrogen atoms in a molecule.

[1] *CRC Handbook of Chemistry and Physics* 97th ed.; Haynes, W.M., Ed.; CRC Press: Boca Raton, FL, 2016; pp. 5–89.