Electronic Supporting Information

Supramolecular Platform Assisted Selective Recognition of Uric Acid with High Sensitivity via Microenvironment Modulation of a Self Assembled Probe

Saikat Samanta, ^a Provakar Paul, ^a Chinmoy Mahapatra, ^b Arunavo Chatterjee, ^c Bibhas Mondal, ^b Ujjal Kanti Roy, ^b Tapas Majumdar *^a and Arabinda Mallick, *^b

^aDepartment of Chemistry, University of Kalyani, Nadia, West Bengal, India – 741235. ^bDepartment of Chemistry, Kazi Nazrul University, Asansol, West Bengal, India – 713340. ^cDepartment of Chemical Sciences, Indian Institute of Science Education and Research (IISER)–Kolkata, Mohanpur, West Bengal, India – 741246.

E-mail: <u>bampcju@yahoo.co.in</u>; <u>atapasmju@gmail.com</u>

Table of Contents

Serial	Content	Figure/Table	Page
No.		No.	No.
1.	Materials		3
2.	Experimental Methods		3
3.	Quenching experiment with CuA	Fig. S1	3
4.	Lifetime plot of BIPM	Fig. S2	4
5.	Table for time-resolved decay parameters	Table S1	4
6.	Emission spectra of BIPM in presence and absence of UA	Fig. S3	4
7.	Absorption spectra of BIPM in absence and presence of UA	Fig. S4	5
8.	Plot of d[FI]/d[CTAB] for gradual CTAB addition in presence of	Fig. S5	5
	UA		
9.	DLS studies	Fig. S6	5
10.	Table for uric acid sensors	Table S2	6–8
11.	Emission of BIPM-CTAB & BIPM-CTAB mixture at different	Fig. S7	8
	time intervals		

Materials

All the solvents (acetonitrile, water) used in the experiments were ofspectroscopic grade and purchased from Spectrochem (India). Cetyltrimethylammonium bromide, Uric Acid, were purchased from TCI (India) and HEPES buffer from Sigma-Aldrich (USA). All the other chemicals were purchased from TCI (India) and used as received. BIPM was synthesized as mentioned elsewhere.¹³ The stock solution of BIPM was prepared in acetonitrile with a concentration of 5 mM. For the additions of surfactant within the BIPM solution, the mixtures were stirred well for 5 mins employing a magnetic stirrer and kept still for ~2 mins to achieve homogeneous and thermally equilibrated solutions required for spectroscopic measurements. HEPES buffer was prepared in doubly distilled de-ionized water using standard protocol and maintaining pH at ~ 7.4.

Experimental Methods

Steady-state spectroscopic measurements

The steady-state absorption and emission spectra were recorded on UH-5300 (Hitachi, Tokyo, Japan) spectrophotometer and F-7000 (Hitachi, Tokyo, Japan) spectrofluorometer, respectively. The F-7000 spectrofluorometer was housed with a 150 W xenon lamp as source and L-type single excitation and single emission monochromator setup. Throughout the steady-state fluorescence measurements, the slit ratio was kept 1 (Ex slit = 5 nm, Em slit = 5 nm). The emission spectrum is scanned from 300 to 600 nm with a scan speed of 1200 nm.min⁻¹. The photomultiplier voltage is set at 400 V. The steadystate fluorescence anisotropy measurements were performed on a Horiba Fluoromax-4 (Jobin Yvon, California, USA) spectrofluorometer where the excitation and emission slits were kept 6 nm.

Time-Resolved emission measurements

A Horiba Jobin Yvon Fluorocube instrument was employed to perform time-resolved emission measurements. A 280 nm excitation source with 1 ns IRF was employed during the decay measurements. The monitoring wavelength was set at the corresponding emission maxima of BIPM at different environment. For the lifetime measurements, the time-correlated single photon counting (TCSPC) method was considered. For the fitting of decay curves, the nonlinear least-squares iterative reconvolution procedure using IBH DAS6 (Version 2.2) was employed using suitable exponential decay equations. The near-unity χ 2 values assessed the goodness of fittings.

Field emission scanning electron microscopy (FESEM)

The FESEM images were taken in a Carl Zeiss SUPRA 55VP field emission scanning electron microscope. 20 μ L of the aqueous solutions of required concentration for each sample were drop casted on a silicon wafer and dried prior to the imaging.



Fig. S1 Plot of $(F_0/F_i) - 1$ vs $[Cu^{2+}]$ for BIPM–CTAB mixture in water. [BIPM] = 30 μ M, λ_{ex} = 280 nm, Temp. 298K.



Fig. S2 Lifetime decay plot of BIPM in presence of CTAB and CTAB–UA mixture in water. [BIPM] = 30 μ M, λ_{ex} = 280 nm, Temp. 298 K.

Table S1. Time-Resolved Decay Parameters of BIPM on Excitation at 280 nm and Monitoring at respective EmissionMaxima, Temp. 298K.

System	τ ₁ , ns	A ₁	τ ₂ , ns	A ₂	τ _{av} , ns	χ²	r	τ _c , ns
BIPM*	0.25	70.27	1.36	29.73	1.02	1.27	0.21	1.10
BIPM + CTAB (1.3 mM)	1.45	9.59	5.25	90.41	5.14	1.08	0.007	0.09
BIPM + CTAB (1.3 mM) + UA (0.3 mM)	0.81	11.37	5.05	88.63	4.96	1.18	0.075	1.14

* Data taken from Ref. 13.

 $\tau_{av} = \text{average lifetime; calculated using } \tau_{av} = [(A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)]$

r = anisotropy; χ^2 indicates the quality of fittings; τ_c = rotational correlation time, calculated using $\tau_c = (\tau_f \times r) / (r_0 - r)$.



Fig. S3 Steady state emission spectra of BIPM and BIPM–UA mixture in water. [BIPM] = 30 μ M, λ_{ex} = 280 nm, Temp. 298K.



Fig. S4 UV-Vis absorption of UA exclusively and of BIPM in presence of CTAB–UA mixture in water. [BIPM] = 20 μM, Temp. 298K.



Fig. S5 Plot of d[FI]/d[CTAB] for BIPM-CTAB emission in (a) 0.0 mM UA; (b) 0.05 mM UA and (c) 0.10 mM UA respectively, to study the effect of UA on cmc of CTAB. [BIPM] = 30 μ M, λ_{ex} = 280 nm, Temp. 298K.



Fig. S6 Particle size distribution of BIPM aggregates in pure H_2O and in CTAB micellar system, as measured from DLS studies. [BIPM] = 25 μ M; temp. 298 K.

Table S2. Comparison of different Uric acid sensors containing the structure/material of the sensor, method of detection,linear range of detection, detection limit (LOD) and time required.

Serial	System/Molecule	Method of	Linear range	Limit of	Time	Ref.
No.		Detection	of detection	detection	required	
				(LOD)		
		Differential	20 650	45		[64]
1.	2,2 -[1,2-ethanediyibis(hitriloethyildyne)]-bis-		20 – 650 μM	15 µM		[51]
	hydroquinone-modified carbon-nanotube-paste-	Pulse				
	electrode (EBNBHCNPE)	Voltammetry				
		(DPV)				
2.	Ion-exclusion chromatography using HEMA-BIO	HPLC-UV	10 – 500 μM	0.426 μM	~10 mins	[S2]
	1000 SB analytical column					
3.	Nitrogen-doped zinc oxide thin film (ZnO:N) based	Cyclic	50- 1000	40 µM	~1 min	[\$3]
	bio-electrode	Voltammetry	μM			
		(CV)				
4.	A hybrid nanomaterial consisting of 3, 3', 5, 5'-	Colorimetry	1 – 40 μM	0.24 μM	~30 mins	[S4]
	tetramethylbenzidine (TMB) and Ni@MnO $_{\rm 2}$					
5.	Colloidal Gold Nanoparticles (GNP) substrate	Surface-	0 – 3500 μM	110 µM	~30mins	[\$5]
		enhanced				
		Raman				
		Spectroscopy				
		(SERS)				
6.	Poly-(vinylpyrrolidone)-protected gold	Fluorescence	5 – 100 uM	1.7 uM	~60 mins	[56]
	nanonarticles (PVP-AuNPs) and Chondroitin		100 μ//			[00]
	sulfate-stabilized gold nanoclusters (CC-AuNCc) as					
	absorber/fluoronhoro pair					

7.	Pb (II)-based metal-organic nanotube (CD-MONT-	Ratiometric change in Fluorescence Fluorescence	0 – 3.6 μM 2.5 – 9.1 μM	0.00073 μM 4.3 μM	~5 mins	[S7]
	2)					
9.	2-Hydroxybenzimidazole Modified Carbon Paste Electrode [MCPE]	Cyclic Voltammetry (CV)	10 – 70 μM	5.1 μΜ		[\$9]
10.	Agilent TC-C18 Column	HPLC-VWD (Variable Wavelength Detector Method)	0.3 – 600 μM	0.01 μΜ	~ 20 mins	[S10]
11.	Glassy carbon electrode (GCE) modified with copper nanoparticles/ polydopamine–Cu/ graphene to form CuNPs/ Cu (II)-PDA/Gr film	Cyclic Voltammetry (CV)	11.8 – 434 μM	6.2 μM		[S11]
12.	1-H-3-methylimidazolium acetate (ionic liquid, IL)- capped nickel nanoparticles (NiNPs)	Colorimetry	0.01–2.4 μM	0.13 μM	~ 4 mins	[S13]
13.	Blue Emissive Carbon Dots Entrapped in Chromium Metal–Organic Frameworks (Cr-MOF)	Fluorescence	20 – 50 μM	1.3 μM	~ 15mins	[S13]
14.	R- HN EIO EIO EIO EIO EIO EIO EIO EIO EIO EIO	Fluorescence	0 – 90 μM	1.23 μM		[S14]
15.	BIPM–CTAB micellar mixture	Fluorescence	50 – 200 μM	6.09 μM	~3 mins	This repor t

References-

S1) M. Mazloumardakani, H. Beitollahi, B. Ganjipour, H. Naeimi and M. Nejati, *Bioelectrochemistry*, 2009, **75**, 1–8.

- S2) R. Ferin, M. L. Pavão and J. Baptista, Clin. Biochem., 2013, 46, 665–669.
- S3) K. Jindal, M. Tomar and V. Gupta, Analyst, 2013, 138, 4353–4362.
- S4) J. Pal and T. Pal, RSC Adv., 2016, 6, 83738-83747

S5) J. E. L. Villa and R. J. Poppi, Analyst, 2016, 141, 1966–1972.

S6) Y. Liu, H. Li, B. Guo, L. Wei, B. Chen and Y. Zhang, *Biosens. Bioelectron.*, 2017, **91**, 734–740.

S7) N. Dey and S. Bhattacharya, Anal. Chem., 2017, 89, 10376–10383.

S8) X. Xin, M. Zhang, J. Zhao, C. Han, X. Liu, Z. Xiao, L. Zhang, B. Xu, W. Guo, R. Wang and D. Sun, J. Mater. Chem. C, 2017, 5, 601–606.

S9) H. D. Madhuchandra and B. E. Kumara Swamy, *Mater. Sci. Energy Technol.*, 2020, **3**, 464–471.

S10) M. Wu, W. Zhang, X. Shen and W. Wang, Foods, 2021, 10, 2814.

S11) D. P. Quan, B. T. P. Thao, N. V. Trang, N. L. Huy, N. Q. Dung, M. U. Ahmed and T. D. Lam, J. Electroanal. Chem., 2021, 893, 115322.

S12) U. Nishan, W. Ullah, N. Muhammad, M. Asad, S. Afridi, M. Khan, M. Shah, N. Khan and A. Rahim, ACS Omega, 2022, 7, 26983–26991.

S13) O. B. A. Shatery and K. M. Omer, ACS Omega, 2022, 7, 16576–16583.

S14) H. Yao, S.-Y. Li, H. Zhang, X.-Y. Pang, J.-L. Lu, C. Chen, W. Jiang, L.-P. Yang and L.-L. Wang, *Chem. Commun.*, 2023, **59**, 5411–5414.



Fig. S7 Emission intensity of the BIPM-CTAB and BIPM-CTAB-UA mixture at different time intervals, depicting the reproducibility of the results with ± 5% error limit. [BIPM] = 30 μ M; [CTAB] = 2 mM; [UA] = 0.25 mM; λ_{ex} = 280 nm, Temp. 298K.