

Interconnectivity between Surface Reactivity and Self-Assembly of Kemp Elimination Catalyzing Nanorods

Ekta Shandilya,^[a] Basundhara Dasgupta,^[a] and Subhabrata Maiti^{*[a]}

Abstract: Understanding the fundamental facts behind dynamicity of catalytic processes has been a longstanding quest across disciplines. Herein, we report self-assembly of catalytically active gold nanorods that can be regulated by tuning its reactivity towards a proton transfer reaction at different pH. Unlike substrate-induced templating and cooperativity, the enhanced aggregation rate is due to alteration of catalytic surface charge only during reactivity as negatively charged transition state of reactant (5-nitrobenzisoxazole) is formed on positively charged nanorod while undergoing a concerted E2-pathway. Herein, enhanced diffusivity during catalytic processes might also act as an additional contributing factor. Furthermore, we have also shown that nanosized hydrophobic cavities of clustered nanorods can also efficiently accelerate the rate of an aromatic nucleophilic substitution reaction, which also demonstrates a catalytic phenomenon that can lead to cascading of other reactions where substrates and products of the starting reactions are not directly involved.

Living systems ranging from bacteria to birds communicate with each other by colonization, clustering, flocking, etc., to carry out functions for their sustainability.^[1] Myriad of spatiotemporally organized catalytic processes play the central role in emergence of living beings and associated properties.^[2] Thus, comprehending the fundamental facts behind catalysts' behavior can aid scientists and technologists to not only understand natural processes better but also to develop synthetic systems with attractive functions.^[3] Some recent pioneering reports suggest that enhanced diffusion might be one of the central phenomena that catalysts experience during their working time.^[4] Catalysts can also come in close proximity to each other and sometimes form assembly for efficient substrate utilization. Two major natural examples of this are the formation of purinosome (dynamic assembly of multi-enzyme complex near mitochondria during purine starvation) and metabolon (multi-

- [a] E. Shandilya, B. Dasgupta, Dr. S. Maiti Department of Chemical Sciences Indian Institute of Science Education and Research (IISER) Mohali Knowledge City, Manauli 140306 (India) E-mail: smaiti@iisermohali.ac.in
- Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202100450

Chem. Eur. J. 2021, 27, 1–7 Wiley Online Library 1 These are not the final page numbers!

enzyme complex formed in a sequential manner during metabolic pathways). $^{\left[5\right] }$

In very few instances, however, synthetically designed catalytically active nano/microparticles (mostly Janus particles) have been observed to form assembly, like cellular systems.^[6-10] Until now, assembly formation and thereby gain-of-function have mostly been reported for amphiphilic or nanoparticle systems by utilizing chemical fuel which mainly acts in supramolecular fashion, or physical energy sources like light or electric signal that can form assembly by configurational change of building blocks.^[11-13] Templated and co-operative assembly of catalytic building blocks using its substrate have also been reported.^[13-15]

In this paper, we put forward an exciting new class of example where synthetic nanocatalysts can form functional selfassembly where catalytic process plays the central part. Here, cetyltrimethylammonium bromide (CTAB)-functionalized gold nanorods catalyzed Kemp Elimination (KE) reaction (a commonly used model to understand mechanistic intricacies in biotransformation)^[16–19] resulted in transition state mediated enhanced flocking behavior of nanorods during the catalytic conversion period to form larger sized assembly (Figure 1). We have also shown that the hydrophobic nanocavities of assembled nanorods can trap hydrophobic substrates and can enhance the rate of an aromatic nucleophilic substitution reaction.

Firstly, we have synthesized the KE substrate, 5-nitrobenzisoxazole (NBI), which converted to 2-cyano-4-nitrophenol (CNP) under catalytic conditions. Product formation kinetics were monitored at 380 nm (see supporting Information).^[16] Initially, we have studied KE catalysis in presence of both hydrophilic



Figure 1. Schematic representation of the assembling of gold nanorods during the KE catalytic conversion, mediated by the formation of negatively charged transition state on its surface.



(solvents, salts, and buffers at different pH values) and hydrophobic (ranging from CTAB micelle to CTAB-capped gold nanoparticles (GNP), and gold nanorods (GNR)) environment. Generally, presence of polar aprotic solvents, and basic salts, can increase catalytic efficiency by 2 to 4 orders of magnitude.^[17] To start with, we examined KE catalysis rate in presence of different percentage of solvents, like: DMSO, Acetonitrile (ACN), Dioxane, DMF and THF in aqueous media, and some basic salts, like: acetate (AcO⁻), thioacetate (AcS⁻), phosphates (HPO₄^{2–}, PO₄^{3–}) and sulphate (SO₄^{2–}) in 70% DMSO-H₂O. However, maximal activity was observed for 70% DMSO-H₂O system, and phosphates. (Figure S6 and S7 in the Supporting Information).

At nearly neutral pH (6 to 8), KE reaction remains almost ineffective in aqueous media mainly because of the nonpolarity of the substrate, NBI (Figure S17 in the Supporting Information). However, introduction of cationic micelle and vesicles in aqueous media can enhance the activity by 2-3 order of magnitude due to: (i) enhanced solubility of substrate in the hydrophobic domain, (ii) higher concentration of reactive anionic base near the stern layer of the cationic miceller or vesicular system, and (iii) more than 2-fold lower dielectric constant of miceller stern layer compared to bulk water.^[19] In fact, we also observed a similar scenario in simple CTAB miceller system where maximally an almost ~200-fold enhanced activity was observed at 8 mM CTAB concentration (Figure S9 in the Supporting Information). Encouraged by the above-mentioned facts and observations, we decided to utilize GNP (hydrodynamic diameter, $D_{\rm h} = 25 \pm 2$ nm) and GNR with aspect ratio of 2.5 ± 0.5 having width of 6 ± 1 nm synthesized using reported protocols (Figure S10-S12 in the Supporting Information).^[20] Highest initial rate (V_i) in KE catalysis was observed with GNR by almost 50, 200, and 500 -fold in pH=6, 7, and 8, respectively while comparing with buffer only, at our experimental condition $([NBI] = 100 \ \mu M,$ [GNR] = 0.15 nM $([Au] = 100 \ \mu M),$ [Phosphate] = 10 mM (Figure 2a + b). Additionally, the observed activity in GNR is ~2-fold higher than CTAB miceller system and GNP.

Also, the activity was increased with increase in concentration of phosphate buffer from 5–20 mM, pH 8 with GNR at our experimental conditions (Figure 2c). The observed higher activity in GNR is probably due to: (i) presence of sharp edges which are known to show pronounced catalytic effects compared to isotropic ones (edges of GNR contains highly reactive facets like {100} and {110}),^[21] (ii) GNR possesses much higher surface area/volume ratio compared to spherical GNP, therefore GNR contains larger reactive sites,^[21b] and (iii) bilayer attachment of CTAB around the nanoparticle also provide added benefits as mentioned in preceding paragraph.

Next, we performed time-dependent UV-Vis spectroscopic measurement to observe change in surface plasmon resonance pattern of GNR under catalytic conditions. For this purpose, we monitored absorbance at 750 nm (characteristic peak of GNR) during the course of KE catalysis.^[22] For this, we firstly added GNR (0.15 nM, [Au] = 100 $\mu\text{M})$ and water mixture with and without NBI, then after 3 minutes phosphate buffer was added to the system and observed an instant decrease in absorbance value (Figure 3a-3c). At pH 7, a slightly higher decrease in absorbance value was observed than pH 6 in both presence and absence of NBI (Figure S19 in the Supporting Information). While at pH 8, a decrease of 0.035 and 0.01 units in absorbance was observed in presence and absence of NBI, respectively, after only one minute of addition of buffer at our experimental condition. This difference in A750 increased during catalytic activity, suggesting clustering of GNR over time. Again, we have observed a continuous decrease in A_{750} with increase in buffer concentration from 5 mM to 20 mM (Figure S20-S21 in the Supporting Information). While maximum deviation in A750 from initial value was observed for pH 8, 20 mM phosphate buffer at our experimental condition.

Furthermore, we performed dynamic light scattering (DLS) experiments to find out the size of the particles present inside the system with respect to time. Here also, we observed increase in size of GNR in presence of NBI with increase in pH from 6 to 8. The observed *z*-average size of GNR system, after one minute of buffer addition was 39 ± 2 nm, 43 ± 3 nm, and 48 ± 5 nm in absence of NBI, which increased to 42 ± 4 nm,



Figure 2. (a) Comparison of *V*i (Nanoparticle)/*V*i (buffer) at pH 6, 7, and 8 for GNP and GNR. Amount of KE catalytic product formed as a function of time in GNR system at (b) pH 6 to 8, 10 mM phosphate buffer, and (c) 5, 10 and 20 mM of phosphate buffer at pH 8. Experimental condition: [GNP]=0.14 nM ([Au]=100 μ M), [GNR]=0.15 nM ([Au]=100 μ M), buffer=phosphate, [NBI]=100 μ M, T=25 °C.

Chem. Eur. J. 2021, 27, 1–7 www.chemeurj.org 2 These are not the final page numbers! Communication doi.org/10.1002/chem.202100450



Figure 3. Change in A₇₅₀ in presence and absence of NBI at (a) pH 6, (b) pH 7, (c) pH 8 with time. Change in hydrodynamic diameter in absence and presence of NBI at (d) pH 6, (e) pH 7, (f) pH 8 with time. (g) Zeta potential values of GNR system in buffer from pH 6 to 8. (h) Change in zeta potential with time in absence and presence of the reactant (NBI) and the product (CNP) at pH 8. TEM image of GNR (i) in water, (j) without NBI in pH 8, 10 mM phosphate buffer. (k) with NBI at pH 8, 10 mM phosphate buffer. The TEM samples were drop-casted in the TEM grid exactly after 2 minutes of addition of buffer with or without NBI solution. Experimental condition: [GNR] = 0.15 nM ([Au] = 100 μ M), buffer = phosphate, [NBI] = 100 μ M, T = 25 °C.

 45 ± 5 nm, and 65 ± 8 nm in presence of NBI at pH 6, pH 7, and pH 8 respectively at our experimental condition (Figure 3d-3f). The difference between average size of GNR system in absence and presence of NBI increased with time at all pH values, with maximal difference at pH 8 as the catalytic rate is highest in this case. In addition to this, we further observed increase in average size with increase in the concentration of phosphate buffer from 5 mM to 20 mM (Figure S22 in the Supporting Information). This corroboration of UV-vis spectroscopic data and DLS measurements suggest the interconnectivity of catalytic activity and aggregation kinetics. We hypothesize that the aggregation behavior is due the formation of negatively charged transition state (TS) on nanorod surface during KE catalysis and in case of high reaction rate, the concentration of the TS on GNR surface might become high enough to induce the aggregation more effectively (Figure 1). This enhancement in size and KE catalysis in GNR system has also been verified via zeta potential measurements.^[23] Zeta potential of our reaction system ([GNR] = 0.15 nM, [Au] = 100 μ M) decreased from 51 \pm 5 mV, 38 ± 1 mV and 30 ± 3 mV, as we increased pH from 6, 7, and 8 respectively for 10 mM phosphate buffer (Figure 3g). The rate of decrease in zeta potential is significantly higher in presence of NBI and during the period of catalytic conversion rather than the product itself (Figure 3h and S24 in the Supporting Information). These outcomes made us postulate that the negatively charged transition state (TS) formed during KE catalysis resides on nanorod surface and results in decrease of GNR surface potential. As GNR surface potential during reaction time at pH=8 sharply decreased to ~15 mV (below colloidal stability zone)[23] due to accumulation of higher amount of anionic TS on its surface, therefore it showed faster and higher aggregation. The decrease in zeta potential value continued as we increased strength of pH 8, phosphate buffer from 5 mM to 20 mM (Figure 3h and S23 in the Supporting Information). In addition to this, TEM (transmission electron

Chemistry Europe

European Chemical Societies Publishing



microscopy) images also suggested formation of higher degree of self-assembled GNR upon addition of NBI (Figure 3i-k).

We have also studied the reusability of GNR for KE catalysis. For this purpose, we added NBI in batches of 50 μ M and looked at the changes in size of GNR system by using DLS measurements and product formation kinetics by using UV-Vis spectroscopy (Figure S25 in the Supporting Information). The efficiency of KE catalysis in repetitive cycle decreased after addition of each batch, presumably because of the product inhibition effect (Figure S16 in the Supporting Information). It suggests that the product also have affinity on the cationic GNR surface owing to its negative charge along with the hydrophobic residue.

Further, we did motion analysis by optical video recording and MSD (mean squared displacement) calculations to understand the catalytic effect in diffusion.^[24,25] It is worthy to mention that enhanced diffusion of catalyst during reaction are one of the fascinating phenomenon and discussed issues since last decades among interdisciplinary sciences.^[4] Mostly, selfphoretic mechanism (e.g. self-electrophoretic, self-thermophoretic, self-diffusiophoretic etc.) play the prime role behind this effect, although the exact reason still remain dubious.[4f] One of the most reliable technique to measure this phenomenon is by using tracking motion of the particle by optical/fluorescence microscopy.^[24,25] For this, we have used a micro-sized replica of our system formed by using carboxylate modified polystyrene bead (d = 2 μ m) GNR conjugate (PS-GNR) as only GNR (dimension of ~25 nm) cannot be observed under optical microscope (Figure 4a and S26 in the Supporting Information). Encouragingly, we have observed significantly enhanced diffusion (~5-7



Figure 4. (a) Schematic representation of hybridization chamber (containing eight units in one strip) containing PS-GNR solution with microscope setup. The movement of the PS-GNR conjugate was observed under the optical microscope at a resolution of 100× and scan rate of 10 frames/second. (b) Trajectory of PS-GNR conjugate in absence and presence of NBI (100 μ M) over 10 sec in the XY plane observed under optical microscope and analyzed using Tracker software. (b) Diffusion co-efficient of PS-GNR conjugate in absence and presence of NBI (100 μ M) and the catalyzed product, CNP (100 μ M) as obtained from the slope of the MSD curves using MSD =4D Δ t. CI=95% with 8 PS-GNR conjugates from 4 sets of experiment.

fold) of GNR-bead conjugated particles in presence of NBI in comparison with CNP, with NBI in water and in only buffer (Figure 4b+4c, Figure S27-S29 and Table S2 in the Supporting Information). We believe this behavior is due to self-electrophoretic effect as uncharged reactant results slightly charged product resulting momentary imbalance of electrical charge.^[4d] It is noteworthy that micron sized bead which initially remained catalytically inactive, can enhance the diffusion of the whole conjugate, just by its surface functionalization with active nanometer-sized GNR (Supporting video, SV1 in the Supporting Information). In fact, we were able to visualize formation of dimer/trimer of microbeads coated with GNR under catalytic condition (Figure S28 in the Supporting Information). We presume that faster diffusion under catalytic condition can play additional role in higher assembly under catalytic condition as mentioned in earlier literature reports.^[26]

Finally, we were curious to explore if this self-assembly of GNR during KE catalysis can lead to the emergence of additional functionality not directly related to the KE catalysis. We argue that the hydrophobic cavities formed during assembly formation of gold nanorods can be utilized as a nanoreactor where hydrophobic reactants can be trapped and made to react.^[12] To study this dual catalytic behavior of gold nanorods, we chose an aromatic nucleophilic substitution reaction between octyl amine and 4-Chloro-7-nitrobenzofurazan (NBD-chloride) which form a fluorescent adduct (NBD-C₈), where reaction can be monitored easily by fluorescence techniques (Figure S33 in the Supporting Information). This reaction does not proceed in aqueous buffer system, however, in presence of GNR substantial reactivity was observed as the hydrophobic bilayer zone of CTAB on its surface helped the solubilization of the substrates. Interestingly, presence of NBI (100 $\mu\text{M})$ leads to more NBD-C_{8} formation where clustering of GNR is more (Figure 5a+b and S35 in supporting information). Fluorescence microscopic images also showed more and larger sized fluorescent particles (NBD-C₈ adduct formed inside GNRs or in the cavity of its aggregates) in presence of NBI (Figure 5c+d). Interestingly, here also, we have observed an increase in adduct formation with increase in pH from 6 to 8. (Figure S35 in the supporting information). Maximum NBD-C₈ adduct formation was observed for pH 8 in presence of NBI, which again corroborates previous results of GNR aggregation. The formation of $\mathsf{NBD-C}_8$ adduct was ensured by using mass spectrometry (Figure S36 in the Supporting Information).

In summary, we have shown that synthetic catalysts can show enhanced assembly which is driven by the formation of transition state during catalytic conversion. In KE catalysis, uncharged reactant leading to anionic TS and thereby product on the cationic nanocatalyst (GNR) surface leads to decrease in surface potential which results in loss of dispersibility of the colloidal system inducing the aggregation phenomenon. Notably, here neither substrate nor product plays any direct interactive role towards aggregation. Additionally, we have demonstrated a catalytic phenomenon occurring at the surfactant bilayer of the nanoparticle surface can lead to cascading of other reactions, absolutely unrelated to the original catalytic reaction (KE). We believe apart from unraveling



Figure 5. (a) Schematic representation of the aromatic nucleophilic substitution reaction to form a higher amount of fluorescent adduct (NBD–C₈) [excitation/emission maxima = 480/550 nm in buffer and 465/535 nm in GNR containing buffer] inside GNR cluster in presence and absence of NBI. (b) NBD–C₈ formation in absence and after 10 minutes of addition reaction of NBI (100 μ M) in GNR system at pH 6, pH 7, and pH 8. Experimental condition: [NBI] = 100 μ M, [GNR] = 0.15 nM ([Au] = 100 μ M), [Phosphate] = 10 mM, T = 25 °C. Fluorescent microscopic images of reaction mixture in presence of PH 8, 10 mM phosphate buffer and in (c) presence and (d) absence of NBI.

fundamental behavior of catalysts; these results can also potentially lead to the emergence of more life-like complex and dynamic chemical systems with unique multi-dimensional functionality as it showed a completely different approach to generate assembly of a catalytic system which gets fueled during catalytic processes enabling new possibilities for nextgeneration dynamic materials.^[27,28]

Acknowledgements

S.M. acknowledges financial support of Science and Engineering Research Board (SERB) (File No. SRG/2019/000365) and MHRD-STARS grant (File no. STARS/APR2019/CS/284/FS). E.S. acknowledges CSIR, India (09/947(0109)/2019-EMR–I) for doctoral research grant.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Catalysis \cdot enhanced diffusion \cdot gold nanorods \cdot self-assembly \cdot transition states

- S. Camazine, J.-L. Deneubourg, N. R. Franks, J. Sneyd, G. Theraulaz, E. Bonabeau, *Self-Organization in Biological Systems*, Princeton: Princeton University Press, 2001.
- [2] a) S. Aubert, M. Bezagu, A. C. Spivey, S. Arseniyadis, *Nat. Chem. Rev.* 2019, *3*, 706–722; b) D. Kroiss, G. Ashkenasy, A. B. Braunschweig, T. Tuttle, R. V. Ulijn, *Chem* 2019, *5*, 1917–1920.
- [3] a) R. Ye, T. J. Hurlburt, K. Sabyrov, S. Alayoglu, G. A. Somorjai, Proc. Natl. Acad. Sci. USA 2016, 19, 5159–5166; b) T. Patiño, X. Arqué, R. Mestre, L. Palacios, S. Sánchez, Acc. Chem. Res. 2018, 51, 2662–2671; c) A. Altemose, A. J. Harris, A. Sen, ChemSystemsChem 2020, 2, e1900021; d) M. A. Sánchez-Farrán, A. Borhan, A. Sen, V. H. Crespi, ChemSystemsChem 2020, 2, e1900036.
- [4] a) H. Wang, M. Park, R. Dong, J. Kim, Y.-K. Cho, S. Granick, T. Tlusty, *Science* 2020, *369*, 537–541; b) A.-Y. Jee, Y.-K. Cho, S. Granick, T. Tlusty, *Proc. Natl. Acad. Sci. USA* 2018, *115*, E10812-E10821; c) T. S. C. MacDonald, W. S. Price, R. D. Astumian, J. E. Beves, *Angew. Chem. Int. Ed.* 2019, *58*, 18864–18867; *Angew. Chem.* 2019, *131*, 19040–19043; d) H. S. Muddana, S. Sengupta, T. E. Mallouk, A. Sen, P. J. Butler, *J. Am. Chem. Soc.* 2010, *132*, 2110–2111; e) C. Weistuch, S. J. Pressé, *J. Phys. Chem. B* 2018, *122*, 5286–5290; f) Y. Zhang, H. Hess, *ACS Cent. Sci.* 2019, *5*, 939–948.
- [5] a) S. An, R. Kumar, E. D. Sheets, S. J. Benkovic, *Science* 2008, *320*, 103–106; b) B. L. Møller, *Science* 2010, *330*, 1328–1329.
- [6] W. Wang, W. Duan, A. Sen, T. E. Mallouk, Proc. Natl. Acad. Sci. USA 2013, 110, 17744–17749.
- [7] R. Soto, R. Golestanian, Phys. Rev. E 2015, 91, 052304.
- [8] G. Kokot, G. V. Kolmakov, I. S. Aranson, A. Snezhko, Sci. Rep. 2017, 7, 14726.
- [9] E. L. Jewell, W. Wang, T. E. Mallouk, Soft Matter 2016, 12, 2501–2504.
- [10] X. Zhao, H. Palacci, V. Yadav, M. M. Spiering, M. K. Gilson, P. J. Butler, H. Hess, S. J. Benkovic, A. Sen, *Nat. Chem.* **2018**, *10*, 311–317.
- [11] a) S. Maiti, I. Fortunati, C. Ferrante, P. Scrimin, L. J. Prins, *Nat. Chem.* 2016, *8*, 725–731; b) A. Mishra, D. B. Korlepara, S. Balasubramanian, S. J. George, *Chem. Commun.* 2020, *56*, 1505–1508; c) A. Jain, S. Dhiman, A. Dhayani, P. K. Vemula, S. J. George, *Nat. Commun.* 2019, *10*, 450; d) J. Deng, A. Walther, *Adv. Mater.* 2020, *32*, 2002629; e) M. Sawczyk, R. Klajn, *J. Am. Chem. Soc.* 2017, *139*, 17973–17978.
- [12] a) H. Zhao, S. Sen, T. Udayabhaskararao, M. Sawczyk, K. Kučanda, D. Manna, P. K. Kundu, J. W. Lee, P. Král, R. Klajn, *Nat. Nanotechnol.* 2016, *11*, 82–88; b) S. Chandrabhas, S. Maiti, I. Fortunati, C. Ferrante, L. Gabrielli, L. J. Prins, *Angew. Chem. Int. Ed.* 2020, *59*, 22223–22229; *Angew. Chem.* 2020, *132*, 22407–22413.
- [13] a) R. K. Grötsch, C. Wanzke, M. Speckbacher, A. Angi, B. Rieger, J. Boekhoven, J. Am. Chem. Soc. 2019, 141, 9872–9878; b) Pezzato, C. Cheng, J. F. Stoddart, R. D. Astumian, Chem. Soc. Rev. 2017, 46, 5491–5507; c) G. Ragazzon, L. J. Prins, Nat. Nanotechnol. 2018, 13, 882–889.
- [14] H. F. Virgós, A.-N. R. Alba, S. Hamieh, M. C. Delsuc, S. Otto, Angew. Chem. Int. Ed. 2014, 53, 11346–11350; Angew. Chem. 2014, 126, 11528– 11532.
- [15] P. S. Munana, G. Ragazzon, J. Dupont, C. Z.-J. Ren, L. J. Prins, J. L.-Y. Chen, Angew. Chem. Int. Ed. 2018, 57, 16469–16474; Angew. Chem. 2018, 130, 16469–16474.
- [16] a) A. Li, B. Wang, A. Ilie, K. D. Dubey, G. Bange, I. V. Korendovych, S. Shaik, M. T. Reetz, *Nat. Commun.* **2017**, *8*, 14876; b) F. Hollfelder, A. J. Kirby, D. S. Tawfik, K. Kikuchi, D. Hilvert, *J. Am. Chem. Soc.* **2000**, *122*, 1022–1029; c) S. Rani, B. Dasgupta, G. K. Bhati, K. Tomar, S. Rakshit, S. Maiti, ChemBioChem **2021**, *22*, 1285–1291.
- [17] M. L. Casey, D. S. Kemp, K. G. Paul, D. D. Cox, J. Org. Chem. 1973, 38, 2294–2301.
- [18] H. K. Privett, G. Kiss, T. M. Lee, R. Blomberg, R. A. Chica, L. M. Thomas, D. Hilvert, K. N. Houk, S. L. Mayo, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 3790– 3795.
- [19] a) J. Pérez-Juste, F. Hollfelder, A. J. Kirby, J. B. F. N. Engberts, Org. Lett. 2000, 2, 127–130; b) E. Sanchez, S. Lu, C. Reed, J. Schmidt, M. Forconi, J. Phys. Org. Chem. 2016, 29, 185–189.
- [20] a) N. R. Jana, Small 2005, 1, 875–882; b) S. Maiti, M. Ghosh, P. K. Das, Chem. Commun. 2011, 47, 9864–9866.
- [21] a) M. A. Mahmoud, R. Narayanan, M. A. El-Sayed, Acc. Chem. Res. 2013, 46, 1795–1805; b) S. G. Jiji, K. G. Gopchandran, Colloids Interf. Sci. Commun. 2019, 29, 9–16; c) B. Ni, X. Wang, Adv. Sci. 2015, 2, 1500085.
- [22] R. Kanjanawarut, B. Yuan, S. Xiao, Nucleic Acid Ther. 2013, 23, 273-280.
- [23] R. J. Hunter, Zeta Potential In Colloid Science: Principles And Applications, Academic Press, UK, 1988.
- [24] X. Ma, A. Jannasch, U.-R. Albrecht, K. Hahn, A. Miguel-López, E. Schäffer, S. Sánchez, *Nano Lett.* 2015, *15*, 7043–7050.



- [25] S. Ghosh, F. Mohajerani, S. Son, D. Velegol, P. J. Butler, A. Sen, *Nano Lett.* 2019, 19, 6019–6026.
- [26] a) S. A. Mallory, C. Valeriani, A. Cacciuto, Annu. Rev. Phys. 2018, 69, 59– 79; b) M. N. Popescu, Langmuir 2020, 36, 6861–6870.
- [27] a) J. Ottelé, A. S. Hussain, C. Mayer, S. Otto, *Nat. Can.* 2020, *3*, 547–553;
 b) B. A. Grzybowski, K. Fitzner, J. Paczesny, S. Granick, *Chem. Soc. Rev.* 2017, *46*, 5647–5678.
- [28] a) C. Wanzke, A. Jussupow, F. Kohler, H. Dietz, V. R. I. Kaila, J. Boekhoven, ChemSystemsChem 2019, 2, e1900044; b) R. Merindol, A. Walther, Chem. Soc. Rev. 2017, 46, 5588–5619; c) E. Shandilya, S. Maiti, ChemSystem-

sChem 2020, 2, e1900040; d) S. Maiti, I. Fortunati, A Sen, L. J. Prins, Chem. Commun. 2018, 54, 4818–4821; e) R. Merindol, A. Walther, Chem. Soc. Rev. 2017, 46, 5588–5619.

Manuscript received: February 4, 2021 Accepted manuscript online: March 26, 2021 Version of record online:

COMMUNICATION

Self-powered assembly: Synthetic functional assembly of catalytic unit (gold nanorod), principally regulated through their surface catalytic reactivity towards proton transfer reaction is reported. The hydrophobic cavities formed during flocking of gold nanorods has been utilized as reactors for hydrophobic substrates towards aromatic nucleophilic substitution reaction in aqueous media, demonstrating a catalytic cascading which is completely unrelated to primary reaction products.



E. Shandilya, B. Dasgupta, Dr. S. Maiti* 1 – 7

Interconnectivity between Surface Reactivity and Self-Assembly of Kemp Elimination Catalyzing Nanorods