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Time Resolved Spectroscopic Studies on a Novel Synthesized Photo-Switchable Organic Dyad and Its Nanocomposite Form in Order to Develop Light Energy Conversion Devices

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UV-vis absorption, steady state and time resolved spectroscopic investigations in pico and nanosecond time domain were made in the different environments on a novel synthesized dyad, 3-(2methoxynaphthalen-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (MNTMA) in its pristine form and when combined with gold (Au) nanoparticles i.e., in its nanocomposite structure. Both steady state and time resolved measurements coupled with the DFT calculations performed by using Gaussian 03 suit of software operated in the linux operating system show that though the dyad exhibits mainly the folded conformation in the ground state but on photoexcitation the nanocomposite form of dyad prefers to be in elongated structure in the excited state indicating its photoswitchable nature. Due to the predominancy of elongated isomeric form of the dyad in the excited state in presence of Au Nps, it appears that the dyad MNTMA may behave as a good light energy converter specially in its nanocomposite form. As larger charge separation rate ($k_{CS} \sim 4 \times 10^8 \text{ s}^{-1}$) is found relative to the rate associated with the energy wasting charge recombination processes ($k_{CR} \sim 3 \times 10^5 \text{ s}^{-1}$) in the nanocomposite form of the dyad, it demonstrates the suitability of constructing the efficient light energy conversion devices with Au-dyad hybrid nanomaterials.

Keywords: Hybrid Nanocomposite, The Dyad, Au Nanoparticles, Time Resolved Spectroscopy, Charge Separation, Charge Recombination, Light Energy Converter.

1. INTRODUCTION

In recent years it has become a great challenge to researchers to explore the solution of energy crisis which is the key scientific problem in 21st century. Production of hydrogen gas,¹ a promising future fuel and the studies on artificial photosynthesis^{2–9} are the most important researches going on today. Apart from this type of research, a number of other promising approaches, have appeared in recent years for working on artificial

photosynthesis based on development of organic molecular systems which will provide nonradiative processes through photosensitized reactions like excitational energy transfer and photoinduced electron transfer (PET) processes. Some novel chemical approaches are being attempted lately to design model compounds of artificial photosynthesis.^{10–15} We could claim these donor–acceptor linked systems are artificial photosynthetic systems in true sense as neither of the redox components is present in natural photosynthesis where chlorophyll special pair is present with quinones. Moreover to avoid much of the complexity of the natural photosynthetic apparatus, many workers in this

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field restricted their focus to design the organic systems for the artificial light energy conversion where the survival duration of the charge separated products resulted from photoinduced charge separation reactions would be enhanced by retarding the energy wasting charge recombination process. This has been done successfully by combining the short chain organic dyads with semiconductor nanoparticles.¹⁶ So, low-cost and at the same time energyefficient light energy conversion devices like components of molecular photovoltaic cells, organic solar cells would be helpful to every individual and the society as a whole to fight against energy crisis.

Recent work provides us the new information about the ingenious properties of nanoparticles as well as core–shell or hybrid nanocomposites^{16–19} in building materials where the light (or solar) energy could be stored and potentially utilized.

A better understanding of the various properties of these nanostructures is needed in order to realize their full potentials in the field of storage of energy. Our present and future investigations are directed in this way along with the other researchers.^{20–31}

Recently we have synthesized a novel dyad (Fig. 1(a)) where the donor methoxynaphthalene is linked by a short chain with an acceptor *p*-methoxyacetophenone.

UV-vis absorption, steady state and time resolved spectroscopic investigations were made in the different



Figure 1. (a) Novel short chain dyad MNTMA; (b) high resolution transmission electron micrograph (HRTEM) picture of the Au nanoparticles (32 nm Gold nanoparticles, there is a size variation ranging from 29 nm to 37 nm).

environments on this novel synthesized dyad in its pristine form and when combined with gold (Au) nanoparticles i.e., in its nanocomposite form. In the present work the primary aim was to determine the rates associated with charge-separation and energy destructive charge recombination processes by using the steady state and time resolved spectroscopic techniques. The experimental data would help to reveal the suitability of the novel dyad to acting as an artificial light energy conversion device. Attempts were made to explore the better suitability of the dyad whether in its pristine or nanocomposite form to acting as a potential energy storage. In this article the experimental details along with the results observed from the steady state and time resolved spectroscopic techniques and their interpretations in the light of the development of efficient light energy conversion devices have been presented and discussed.

2. EXPERIMENTAL DETAILS

2.1. Materials

The method of synthesis and characterization of the dyad 3-(2-methoxynaphthalen-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (MNTMA) is given below in the Section 2.3.

The solvents acetonitrile (ACN) (SRL), and cyclohexresolved different ing the standard procedures and tested before use for the absence of any impurity emission in the concerned American Swavelength region. β -Cyclodextrin (β CD) (Aldrich) and methanol (MeOH) (E Merck, Germany) of spectroscopic grade were used as received. Water was deionized using a Millipore Milli-Q system. The solutions were prepared by dissolving the appropriate amount of β CD in water. Because of the low solubility in water, the dyad was dissolved in pure MeOH and added to the water solution of β CD. The final methanol concentration in a mixture was 0.2% (v/v).

2.2. Spectroscopic Apparatus

Steady state UV-vis and fluorescence emission spectra of dilute solutions $(10^{-4}-10^{-6} \text{ M})$ of the dyad were recorded at the ambient temperature (296 K) using 1 cm path length rectangular quartz cells by means of an UV-vis absorption spectrophotometer (Shimadzu UV-vis 2101PC) and F-4500 fluorescence spectrophotometer (Hitachi), respectively. Fluorescence lifetime measurements were carried out by using the time correlated single photon counting (TCSPC) method using HORIBA JOBIN YVON FLUO-ROCUBE. The quality of fit was assessed over the entire decay, including the rising edge, and tested with a plot of weighted residuals and other statistical parameters e.g., the reduced χ^2 and the Darbin–Watson (DW) parameters. The time resolution is ~ 20 ps and the excitation wavelength used was 375 nm with a diode laser. In some cases NANOLED 280 was used for excitation with 280 nm light.

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The femtosecond-resolved fluorescence decays were measured using a femtosecond upconversion setup (FOG 100, CDP). The samples were excited at 375 nm using the second harmonic of a mode-locked Ti-sapphire laser with an 80 MHz repetition rate (Tsunami, Spectra Physics), pumped by 10 W Millennia (Spectra Physics). The fundamental beam was frequency doubled in a nonlinear crystal (1 mm BBO, $\theta = 25^{\circ}$, $\varphi = 90^{\circ}$), θ and φ being the polar and azimuthal angles. Using a gate pulse of the fundamental beam, the fluorescence emitted from the sample was upconverted in a nonlinear crystal (0.5 mm BBO, $\theta = 10^{\circ}$, $\varphi = 90^{\circ}$). The upconverted light was dispersed in a double monochromator and detected using photon counting electronics. The instrument response time was determined from the cross-correlation function due to sum frequency generation between gate and excitation pulses. The crosscorrelation function was obtained using the Raman scattering from water, displaying a full width at half maximum of approximately (FWHM) of 165 fs. The observed femtosecond resolved decays were fitted using a Gaussian shape for the exciting pulse.

Nanosecond laser flash photolysis set up (Applied Photophysics) containing Nd:YAG (Lab series, Model Lab 150, Spectra physics) laser was used for the measurement of transient absorption spectra. The sample was excited at 355 nm (FWHM = 8 nm) laser light. The other details are given elsewhere.¹⁸

All the solutions prepared for room temperature measurements were deoxygenated by purging with an argon gas stream for about 30 minutes.

2.3. Synthesis and Characterization of the Organic Dyad (E)-3-(2-methoxynaphthalen-1-yl)-1-(4methoxyphenyl)Prop-2-en-1-One (MNTMA)

Synthesis of (E)-3-(2-methoxynaphthalen-1-yl)-1-(4-meth-oxyphenyl)prop-2-en-1-one (**3**).

To a solution of 2-hydroxynapthaldehyde **1** (3.0 g, 17.4 mmol) in anhydrous acetone (30 mL) was added anhydrous K_2CO_3 (2.97 g, 21.5 mmol) and methyliodide (5.43 g, 38.2 mmol) and the resulting mixture was heated to 45 °C (bath temperature) under argon for 2 hours. After completion of the reaction (monitored by TLC), the solvent was removed *in vacuo* and the residue worked up in the usual way using ethyl acetate and water to yield the crude 2-methoxynapthaldehyde (3.0 gm). The crude **2** was used for the next step without further purification.

The crude product **2** from the previous step was taken in a RB flask and dissolved in MeOH (30 mL) followed by addition of 4-methoxyacetophenone (2.42 g, 16.1 mmol) and NaOH (2.1 g, 5 mmol). The mixture was then refluxed for 3 hours after which the reaction was found to be completed as monitored by TLC. The reaction mixture was then cooled and the MeOH evaporated *in vacuo*. The resulting mixture was worked up by addition of water followed by extraction with ethyl acetate (3×50 mL). The combined

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ethyl acetate layers were washed with brine till neutral, after which it was concentrated *in vacuo*. The residue was then chromatographed over a column of silica-gel (60–120 mesh) using 10% ethyl acetate-petroleum ether as eluent to afford the (*E*)-3-(2-methoxynaphthalen-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (**3**, 3.1 g, 56%). M.p. 100–102 °C; ¹H-NMR (400 MHz, CDCl₃): 3.83 (*s*, 3H), 3.99 (*s*, 3 H), 6.96 (*d*, *J* = 9 Hz), 7.26 (*d*, *J* = 9 Hz), 7.36 (dd, *J* = 8, 8 Hz), 7.51 (dd, *J* = 8, 8 Hz), 7.76 (*d*, *J* = 9 Hz), 7.82 (*d*, *J* = 9 Hz), 7.89 (*d*, *J* = 16 Hz), 8.07 (*d*, *J* = 9 Hz), 8.26 (*d*, *J* = 9 Hz), 8.48 (*d*, *J* = 16 Hz); ¹³C-NMR (75 MHz, CDCl₃): 55.6, 56.4, 112.9, 113.9, 117.7, 123.6, 124.0, 127.3, 127.5, 128.7, 129.1, 131.0, 131.6, 131.7, 133.1, 137.1, 157.0, 163.4, 189.7.

2.4. Preparation of Gold (Au) Nanoparticles of Diameter 32 nm

Au nanoparticles were synthesized by the standard procedure adopted by Fren et al.³² In a flux 50 ml deionized water is added with 1.25 ml of 0.01 Molar Chloroauric acid (HAuCl4) and then heated to boiling. After that 625microliter of 1% trisodium citrate (1% = 1 gm)trisodium citrate in 100 ml distilled water) was added with vigorous shaking. The solution changes colour, and turns red indicating the formation of nanoparticles. We keep it boiling for another 5-10 min keeping the volume level of liquid same in the flux. After that the liquid cools down to room temperature. The high resolution Transmission Electron Micrograph (HRTEM) was used to measure the size of the Au nanoparticles (HRTEM picture of Au nanoparticles is shown below in Fig. 1(b)). Average size of Au nanoparticles is found to be around 32 nm diameter, there is a size variation ranging from 29 nm to 37 nm diameter.

2.5. Theoretical Computations

All DFT calculations were performed using Gaussian 03 suit of software operated in the linux operating system. Becke's three parameter hybrid exchange (B3) and Lee–Yang–Parr correlation functional(LYP) were used for the DFT calculations. The geometry optimization and HOMO–LUMO surfaces were obtained from B3-LYP/6–311 g (d, p) level of theory.

3. RESULTS AND DISCUSSION

The present investigation is being carried out in continuation with our previous studies^{10, 12, 13, 18} on photoinduced electron transfer reactions within organic dyad systems consisting of donor and acceptor moieties joined by various types of short spacers. This dyad (Fig. 1) has been chosen to make our studies on similar systems comprehensive.

The modifications consist of (a) shifting the acceptor moiety attached to the spacer to the ortho-position of the methoxy group rather than in the position para-to it and (b) modification of the structure of the "acceptor" part of the dyad. The modification of the relative disposition of Time Resolved Spectroscopic Studies on a Novel Synthesized Photo-Switchable Organic Dyad

the moieties viz. 1,2-rather than 1,4-position was introduced to bring geometrical constraint and for examining its effect on the energy wasting charge recombination process. The chlorine atom present in the benzene ring of the acceptor part of the dyad earlier examined¹⁷ by us was replaced by methoxy group. It is known that the methoxy group displays an electron attracting inductive effect and electron donating mesomeric effect. When present in the para position to a reactive center, it is the donor property which predominates. The donor property of a functional group manifests itself through delocalization of lone pair of electrons through conjugated π -system. An essential criterion for delocalization is that the whole π -system should be planar. The idea behind the bringing of the two components of the dyad closure together was to introduce a geometrical constraint resulting in the destruction of the planarity. This should result in the electron-withdrawing inductive effect of the methoxy group gaining upper hand over its electron donating mesomeric effect. This proposition was corroborated from the theoretical and experimental observations (vide infra). It is known that the methoxy group, when present as a substituent in an aromatic ring can exert both electron donating R effect and electron withdrawing I effect. The former gets upperhand when it is in the position para-to the reactive side chain as evident from the negative Hammett σ value (-0.27). However, the prerequisite for delocalization of electron and the consequent manifestation of R effect is that the molecule should be planar. As evident from theoretical calculation, the dyad molecule is not planar. The electron attraction by the carbonyl group would have been attenuated had the methoxy group exerted its electron donating effect. Since this is not the case, the acetophenone part of the dyad, as a whole behaves as electron acceptor, which actually reflects in Figure 2 (LUMO surface).

3.1. Theoretical Approach

Theoretical computations were done on the optimized ground state geometry of the dyad and the HOMO–LUMO surface by using B3-LYP/6-311g(d,p) level of theory (for details, see Section 2.5). Figure 2 reproduces the HOMO and LUMO surfaces of the dyad.

The optimized structure (Fig. 2) clearly shows the nonplanar geometry of the ground state dyad. As it was seen from the Figure 2, though in HOMO orbital the electron cloud is localized on the donor part but in LUMO hyper surface the electron cloud shifts from the donor to the acceptor sites via the spacer. This indicates the dyad is of donor–spacer–acceptor type and hence methoxy group attached in the benzene ring of the acetophenone side should be acting here as acceptor group due to non-planarity structure (similar to the folded type) of the ground state dyad. Further, spectroscopic investigations strengthening the views made from the theoretical approaches have been described below.



Figure 2. HOMO (left) and LUMO (right) surfaces of optimized geometry of the dyad.

3.2. Steady State and Time Resolved Spectroscopic Measurements on the Dyad in Its Pristine and Nanocomposite Forms

When the unlinked donor methoxynaphthalene (MNT) and the acceptor *p*-methoxy acetophenone (MA) of the present dyad (MNTMA) interact with each other, the UV-vis spectra show only the superposition of the corresponding spectra of the individual redox components. This indicates the lack of ground state complex formation. But when the donor MNT is linked with the acceptor MA via a short spacer (Fig. 1), i.e., when the dyad is formed, a broad absorption band, as expected, is observed in CH solvent spanning between 350 to 400 nm peaking at around 370 nm region (Fig. 3). The band is found to be of charge transfer (CT) nature as confirmed from the observed red shift with the increase of the polarity of the surrounding solvent.

This observation corroborates our proposition made from the theoretical analysis that methoxy functionality attached with the benzene ring of the acetophenone side behaves as an electron accepting group. On excitation of the CT absorption band, a CT fluorescence spectrum was



Figure 3. UV-vis absorption spectra of MNTMA in (1) CH, (2) ACN.



Figure 4. CT fluorescence band of the dyad (MNTMA) with $\lambda_{exe} = 375$ nm. 1: CH; 2: ACN.

obtained at around 450 nm region (Fig. 4). This band undergoes expectedly large bathochromic (red) shift with increase of the polarity of surrounding solvent from CH ($\varepsilon_s \sim 2$) to ACN ($\varepsilon_s \sim 37.5$).

Thus, when the donor and acceptor are present within an intramolecular system (such as dyad), the alignment of both the chromophoric units are such that the formations of CT absorption as well as CT fluorescence bands will be facilitated. The similar observations were made before for similar type of dyad systems^{13, 17} where the acceptor part was *p*-chloroacetophenone (PCA).

From fluorescence lifetime measurements it was observed that (Table I) when CT absorption band is excited (~375 nm), mainly two lifetimes, one is the fast component (~ps order) and the other due to longer lived species or conformation (in ns order) were observed (Table I, Figs. 5(a) and (b), Fig. 5(b) is for picoseconds lifetime measurements done by femtosecond upconversion process to confirm ps species observed from the TCSPC measurements of the decay of the Fig. 5(a)).

However, from fractional contribution, f_i , it is apparent that ps contribution is negligibly small and the decays

from the entire fluorescence emission band envelop (different monitoring wavelengths were used) originate primarily from one species whose lifetime is about 3 ns (Table I). In triple exponential fitting of the decay, when the excitation was made in the CT fluorescence by using 375 nm wavelength, the components of 1 ns and ps species are observed to be much smaller than 3 ns lifetime species. However, it has been shown below that ps component gradually becoming dominating component when the dyad combined with gold nanoparticles. In such a situation also 1 ns component remains significantly small relative to the other two components: one of ps and other 4 ns, as apparent from the corresponding fractional contributions. This 1 ns component seems to be due to the quenched donor part as its presence was clearly observed with the unquenched donor Methoxynaphthalene ($\tau \sim 11$ ns) when the dyad was excited in the donor region (~ 280 nm, Table I). When the CT absorption was excited by using 375 nm light, this 1 ns component becomes significantly small, since this CT band resides in the longer wavelength region, far away from the absorption domain of the donor molecule (~ 280 nm). The situation becomes entirely different when the dyad is combined with gold nanoparticles. Here on 375 nm excitation, ps order emitting species significantly develops at the expense of the longer lived ones (~ 4 ns) (Table I), especially at the longer wavelength side (\sim 550 nm) of the CT emission band. In Figure 5(b) the fluorescence upconversion profile shows significantly the picosecond component and does not exhibit the long-lived ns emission (3-4 ns). This finding is consistent with that observed from TCSPC measurements where relatively larger fractional contribution of the ps species ($\sim 85\%$) than the longer-lived ns component (12%) at 550 nm region (Table I) of the CT fluorescence band, specially when the dyad combined with gold nanoparticles, is apparent.

The steady state CT emission spectra of the dyad exhibit the similar effect in presence of the gold nanoparticles as it was apparent from time resolved measurements. A development of a band at the longer wavelength side (~ 500 to

Table I. Time resolved fluorescence data of the dyad MNTMA in absence and presence of noble Au nanoparticles at the different excitation and emission wavelengths at the ambient temperature.

Conc Au Np (mol dm ⁻³) or presence of β CD	$\lambda_{\rm exc}/{\rm nm}$	$\lambda_{\rm em}/{\rm nm}$	$ au_1$	f_1	$ au_2/\mathrm{ns}$	f_2	$ au_3/\mathrm{ns}$	f_3	χ^2	$k_{\rm cs}/{\rm s}^{-1}$
0	280	358	1.8 ns	0.22	11.0	0.78			1.05	4.6×10^{8}
	375	448	25 ps	0.05	1.1	0.03	3.0	0.92	1.12	
		460	28 ps	0.04	1.2	0.06	3.0	0.90	1.11	
		500	_	_	_	_	3.1	1.0	1.08	
		550	-	_	-	-	3.0	1.0	1.10	
$\times 10^{-5}$ (Au)	280	358	1.9 ns	0.11	10.6	0.89			1.09	4.3×10^{8}
	375	450	30 ps	0.05	1.3	0.03	4.2	0.92	1.11	
		530	35 ps	0.55	0.8	0.02	4.2	0.43	1.09	
		550	30 ps	0.85	0.6	0.03	4.1	0.12	1.02	
β CD	375	500	38 ps	0.26	_	_	4.14	0.74	1.05	
		530	39 ps	0.38	_	_	4.10	0.62	1.05	
		550	39 ps	0.50	-	-	4.10	0.50	1.12	





Figure 5. (a) Fluorescence decay of the dyad (red) in ACN $\lambda_{ex} = 375 \text{ nm}$, $\lambda_{em} = 500 \text{ nm}$, the fast (blue) decaying component represents impulse response (diode laser) ($\chi^2 \sim 1.08$); (b) Picosecond lifetime measurements by femtosecond upconversion technique (see details in the experimental section) (deconvolution of the decay shows the magnitude of the fluorescence lifetime component is ~11 ps at 550 nm of the CT fluorescence produced by excitation with 375 nm light (second harmonic of Ti: Sapphire laser). (Sample was MNTMA dyad combined with Au nanoparticles).

550 nm) of the CT fluorescence is clearly observed when the dyad combined with gold nanoparticles (Fig. 6(a)).

Thus in nanocomposite form of the dyad, comparing the time resolved spectra with the steady state one, it is apparent that another new emitting species is formed whose lifetime is of the order of picosecond (ps). The decrement of fractional contribution associated with the longer lifetime component with concomitant increase of the contribution of ps one as one approaches to the red region of the emission band, provides us the supporting evidences in favor of generation of the new excited conformers in nanocomposite systems at the expense of the

Figure 6. (a) CT fluorescence spectra of the dyad in presence of Au nano particle Without nano particle, (2) with Au nano particle (conc. 8×10^{-6} M); (b) CT fluorescence spectra of the dyad in presence of β CD, the conc. (M) being in 1: 0 M; 2: 1×10^{-4} M; 3: 1×10^{-3} M.

4 ns component. This long-lived ns species was primarily observed in case of pristine dyad only. From picosecond lifetime measurements by femtosecond upconversion technique (see details in the experimental section) deconvolution of the decay shows the magnitude of the fluorescence lifetime component is ~ 11 ps at 550 nm of the CT fluorescence (Fig. 5(b)) produced by excitation with 375 nm light (second harmonic of Ti: Sapphire laser). Thus, the presence of an excited state conformer having fast decay component of the order of picosecond, as observable from TCSPC technique, is further confirmed from upconversion technique of femtosecond resolution. As extraction of 25 ps decay time from TCSPC decay profile may not be accurate enough as this falls on the order of the calibration factor or within time resolution, confirmation of 25 ps species was necessary from femtosecond up conversion technique.

To reveal the nature of the fast decaying conformer, which is found to generate effectively in nanocomposite



Scheme 1. Synthesis of dyad 3.

form of the dyad, the steady state intensity and lifetimes of CT fluorescence were measured in presence of β -cyclodextrin (β CD). As it was reported earlier,³³ in presence of β CD due to formation of inclusion complex there will be preponderance of elongated type isomer of a dyad which will be formed from its folded isomers (Scheme 2).

In presence of β CD, the enhancement of 500 nm region of the CT emission band (Fig. 6(b)) of the dyad MNTMA is observed, similar to the findings made with the addition of gold nanoparticles (Fig. 6(a)). Moreover, from fluorescence lifetime measurements (Table I) it was observed that ps components generate, similar to the situation observed when the dyad combines with Au nanoparticles, in presence of β CD and the associated fractional contribution increases in the similar fashion towards the red region of the CT fluorescence band with the simultaneous reduction of the f values of the longer component. Thus, it could be inferred that the shorter (~ps order) component of the fluorescence lifetime should correspond to the elongated isomeric species (E-type) of the dyad and the longer one should correspond to the folded (Z-form) isomeric species. As we have discussed above, the dyad in the ground state possesses primarily folded type species. So the dyad in its nanocomposite form exhibits photoswitchable character and its elongated form produced on photoexcitation should inhibit the energy wasting charge recombination process as in this type of conformation the donor and acceptor being far away from each other suffer lack of overlapping. A slight decrement (though order remains same $\sim 10^8$) in charge separation rate k_{cs} in presence of gold nanoparticles



Scheme 2. "Cis" means folded type (Z-form), "Trans" corresponds to elongated or *E*-type isomeric species

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(last column of Table I) also indicates in favor of formation of extended conformation in this nanocomposite environment.

3.3. Fluorescence Excitation Spectra

The fluorescence excitation spectra of the two fluorescence bands, one at 450 nm (region of primarily Z-type or folded isomer) and the other at 510 nm (region of considerable amount of E-isomer) of the dyad MNTMA in presence of gold nanoparticles were measured and are shown in the Figure 7.

The observed similar excitation spectra, which correspond well to the UV-vis spectra of CT absorption band of the dyad (Fig. 3), demonstrate that both the emitting species (E- and Z-isomers) originate mainly from the ground state Z-isomeric species of the dyad MNTMA. Thus the possibility of formations of some unwanted bi-products in presence of gold nanoparticles appears to be slim.

Thus, this novel synthesized dyad is unique in that respect that the similar short chain dyads, earlier studied, exhibit mainly extended conformers in the ground state and on photoexcitation due to their photoswitchable character becomes of folded nature in the excited states. The situation is just opposite in this particular dyad MNTMA. Its switching over behavior to elongated conformer on photoexcitation in presence of gold nanoparticles, from its folded (*Z*) conformations in the ground state makes it the



Figure 7. Fluorescence excitation spectra of MNTMA dyad in ACN. Montoring emission wavelengths in: 1: 456 nm; 2: 500 nm; 3:510 nm.

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promising candidate for the development of artificial light energy converter and storage device.

Our next approach would be to measure the charge recombination rate by using laser flash photolysis (pumpprobe) technique by using the third harmonic of Nd:YAG laser system as an excitation profile and a probe for monitoring the transients. The transient absorption spectra would be measured at the different delay times between the exciting pulse and the analyzing or probe pulses. Special attention would be taken to analyze the transient absorption spectra and the corresponding absorption decays of the dyad without and in presence of Au nanoparticles i.e., in its pristine and nanocomposite forms.

3.4. Transient Absorption Measurements by Nanosecond Laser Flash Photolysis Technique

The transient absorption spectra of the dyad MNTMA in ACN were measured by the direct excitation of CT absorption band at 355 nm (using the third harmonic of Nd: YAG laser system), without (Fig. 8(A)) and in presence of Au nanoparticles (Fig. 8(B)). From the Figure 8(A), it is apparent that in absence of Au nanoparticles the dyad MNTMA exhibits initially a broad transient band at around 400 nm to 500 nm domain, peaking at about 420 nm with a shoulder at 450 nm region.

With increase of delay times between the exciting and the probe pulses there occurs an intensity inversion nology t between the 420 nm and 450 nm bands (Fig. 8(A)). It is apparent that the 450 nm band is developing at the expense of the 420 nm one. These observations clearly indicate that the two different species are involved. It is confirmed that 420 nm band of MNTMA is responsible for the donor cationic species (MNT⁺). This was confirmed from the artificial production of oxidized species (MNT⁺) of the donor MNT by constant current charger (model DB 300 DB Electronics, India). The donor cation, produced by electrochemical oxidation of MNT was found to absorb at 420 nm region, as observed from the conventional UV-vis absorption spectrophotometer. Following the observations made earlier by Baba et al.³⁴ the 450 nm band could be assigned to the monomeric triplet of the donor MNT.

It can be surmised that the excited singlet CT species formed from the excitation of ground state CT complex undergoes relaxation to the corresponding triplet state by the intersystem crossing (ISC). Since ISC rate generally varies between 10^{11} and 10^8 s^{-1} and as the delays used in the nanosecond laser flash photolysis measurements are of microsecond (μ s) order, so, as expected, no rise time indicating the generation of the triplet at 450 nm region from the charge recombination processes is observed.

From the transient absorption decays of the donor cationic species at 420 nm (Fig. 9) without (pristine) and with the addition (nanocomposite form) of Au nanoparticles, the energy destructive charge recombination rates (k_{CR}) were determined. From the decays it is apparent that



Figure 8. (A) Transient absorption spectra of the dyad MNTMA in ACN at the different delay times (in pristine form) (The μ s delays used are shown at the top right-hand corner); (B) Transient absorption spectra of the dyad MNTMA in ACN at the different delay times in presence of Au nanoparticles (in nanocomposite form).

the decay becomes slower when the dyad combines with the Au nanoparticles. From the analysis of the decays, ionpair lifetime (τ_{ip}) of the dyad was found to be enhanced by 3 times in case of its nanocomposite form relative to its pristine form (from 1.1 μ s to 3 μ s). Thus when the dyad combines with Au nanoparticles, the survival duration of the charge separated species increases. Approximated charge recombination rates were computed ($k_{CR} \sim 1/\tau_{ip}$) and the energy destructive charge recombination rate k_{CR} is found to be slowed down ($3.3 \times 10^5 \text{ s}^{-1}$) in case of Audyad hybrid nanocomposite system in comparison to the pristine form of the dyad ($\sim 9.0 \times 10^5 \text{ s}^{-1}$).

From all the experimental observations it could be inferred that in case of the nanocomposite system as the formations of the elongated conformations of the dyad facilitate in the excited state (in the ground state the dyad shows only folded conformer), the two redox components will be at a far apart position lacking the overlapping between them. This particular geometry will impede the energy destructive charge recombination process between



Figure 9. Comparative analysis of the transient absorption decays of the donor cations at 420 nm (1) without and (2) in presence of Au nanoparticles at the ambient temperature.

the redox components. Thus the survival duration of the charge separated species would be increased what we actually observed above.

In addition to this effect, as the charge separation rate ($\sim 4 \times 10^8 \text{ s}^{-1}$) is much faster than the CR rates ($\sim 3 \times 10^5 \text{ s}^{-1}$) in nanocomposite environment of the dyad, it indicates the possibility of constructing the efficient light energy conversion devices specially with Au-dyad nanocomposite systems. The suitability of constructing light energy conversion device using the Au-Dyad nanocomposite mainly originates from the changed dyad conformations to elongated nature on photoexcitations and the present results seemingly indicate that Fermi level of Au nanoparticles has no significant role in slowing down the charge recombination rate processes unlike our observations made earlier in case of other shortchain dyads.

Our future efforts would be to combine the present organic short-chain dyad with various nanoparticles or core-shell of noble metal and semiconductor nanocomposite systems. In this way efficient and at the same time cost-effective and biocompatible light energy conversion devices could be designed to fight against energy crisis.

4. CONCLUSIONS

From UV-vis absorption, steady state and time resolved spectroscopic measurements coupled with theoretical approaches, it has been inferred that the present short chain dyad MNTMA behaves like a photoswitchable compound, the effect of which becomes more pronounced when combined with noble metal Au nanoparticles. Au-nanoparticles act as very effective tool to recognize the presence of the two emitting isomeric species (elongated and folded) of the dyad though only one conformer of folded nature exists in the ground state. Due to the predominancy of elongated

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isomeric form of the dyad in the excited state in presence of Au Nps, it appears that the dyad MNTMA may behave as a good light energy converter in its nanocomposite form. As the larger charge separation rate ($k_{\rm CS} \sim 4 \times 10^8 \, {\rm s}^{-1}$) is observed relative to the rate associated with the energy wasting charge recombination processes ($k_{\rm CR} \sim 3 \times 10^5 \, {\rm s}^{-1}$) in the nanocomposite form of the dyad, it demonstrates the possibility of constructing the efficient light energy conversion devices with Au-dyad hybrid nanomaterials. Further investigation on the dyad system to design nanocomposite light energy converter using the other nano noble metal silver is underway.

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