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Paradigms Shift When Solvent-less Fluids Come into Play

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Solvent-less organic fluids are a new class of functional soft materials. Here the available fluid matrix makes it equally competitive with the solvent assisted systems. In this Perspective, the ways in which organic fluids challenge the established and accepted paradigms is highlighted. In general, fundamental properties such as photoisomerization, energy/electron transfer, photon upconversion and reversible dioxygen binding are being controlled by solvents and/or solvent polarity, presence of oxygen etc. Here solvent-less fluids challenge the paradigms by realizing it in the neat, solvent-less and ambient condition. This new phase of research has created many potential functional materials, which works better and efficient than the solvent assisted systems. Hence this relatively new research topic and results need special attention. Here we discuss a few representative examples to point out the challenges offered in their functioning.

Introduction

Intra- and intermolecular forces play a significant role in natural as well as artificial functional assemblies and remained as a driving force to design many organic soft materials.[1] However, a new phase called solvent-less fluid materials embodying minimised intermolecular interactions, has been introduced in the recent past.[2] The understanding of this intriguing concept itself is of importance because it challenges the existing paradigm of the role of solvents in controlling the inherent features of the molecules.[3] The potential of these materials in achieving better performance in solvent-less condition has already gathered much attention. This attractive class of material has also exhibited their excellent features upon integrating into electronic devices.[2] The very recent fundamentally and technologically important breakthroughs in this fastly growing research interest need to be acknowledged. Herein the main focus is to highlight the challenges put forward by these functional materials.

In the case of proteins, it has been believed that solvent molecules are essential for establishing and maintaining protein folding. In short, mostly biomolecular activities are highly sensitive to the interplay of solvent-protein interactions. In contrary, Mann and coworkers introduced solvent-less fluid proteins, by utilising ionic interaction between cationic proteins and a flexible corona of anionic polymer surfactant (Fig. 1).[4-6] Myoglobin (Mb) based hybrid nanoconstruct fluid retained near-native structure.[5] The dynamic hyperthermophilic fluid reversibly re-fold in the solvent-less state due to configurational flexibility and molecular interactivity provided by the outer polymeric layer.[6]

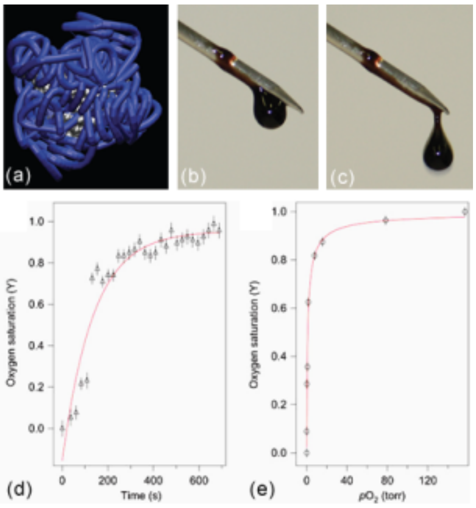

Fig. 1 (a) Graphic showing electrostatic binding of the anionic polymer surfactant to cationised Mb. Photographs showing gravity-induced flow of fluid Mb droplet at 60 °C and under atmospheric pressure after (b) 5 s and (c) 10 s. Plots showing (d) dioxygen binding with time and (e) degree of oxygen saturation against partial pressure of dioxygen of fluid hybrid nanoconstruct at 37 °C. Adapted with permission from ref. 5. Copyright 2010 Macmillan Publishers Limited.

Likely to the characteristic features of haem protein under physiological conditions, fluid Mb reversibly binds gaseous

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ligands such as dioxygen, carbon monoxide and sulphur dioxide molecules at the hememetallocentre (Fig. 1d,e).[5] Such an observation absolutely in the solvent-less condition is hitherto unknown. The equilibrium dioxygen association curve indicated an independent binding and hence no cooperativity in binding (Fig. 1e). However, the diffusional constraints in the viscous solvent-less protein have significantly reduced the rate of ligand binding. This unprecedented and challenging bio-nanomaterial phase questions the established paradigms in protein folding and function, and hence opens a wide area of research.

Nakanishi and co-workers reported white[7] as well as full-colour[8] luminescent solvent-less fluids. A combination of blue emitting room temperature fluid anthracene (Fig. 2a,b) and solid dopants have generated full-colour luminescence at a single wavelength excitation.[8] High fluorescence quantum yield and high photostability, low viscosity etc of fluid anthracene made the composite feasible. An efficient energy transfer between fluid anthracene and varying amounts of 9,10-bis(phenylethynyl)anthracene (**1**) assisted fluorescence colour tuning from blue to cyan (0.3 mol%), green (0.5 mol%), greenish yellow (2 mol%) and finally to yellow (5 mol%) (Fig. 2c). Similarly, addition of tris(1,3-diphenyl-1,3-propanedionato)(1,10-phenanthroline)europium (III) (**2**) has changed the blue fluorescence of fluid anthracene to violet (2 mol%) and purple (5 mol%) colours (Fig. 2c). A thermoresponsive composite of fluid anthracene, 0.5 mol% and 5 mol% of the dopants, respectively, exhibited red emission colour at room temperature. It has been changed to yellow (50 ˚C) and emerald green (100 ˚C) with temperature (Fig. 2c). Such an effective luminescence colour tuning has lead to the development of technologically important emissive fluid materials.

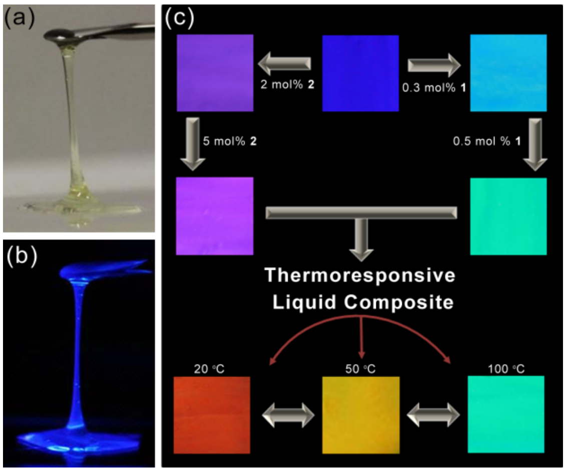

Fig. 2 Photographs of solvent-less fluid anthracene under (a) visible and (b) 365 nm UV light and (c) the overall fluorescence colours from fluid anthracene composites. Adapted with permission from ref. 8. Copyright 2013 Macmillan Publishers Limited.

Recently, triplet-triplet annihilation (TTA) based upconversion (UC) systems have raised much research interest.[9] However, so far efficient upconversion has been achieved mostly in solution due to the essential diffusion of triplet molecules for energy transfer.[10] In addition, the presence of molecular oxygen, which deactivates the triplet states, significantly limits UC.[9] A fluid photon upconverting system consists of triplet sensitizer Pt(II) porphyrin as a donor (D) dopant and 9,10-diphenylanthracene based fluid acceptor (A) functioning in-air is reported.[11] The composite (D/A = 0.01 mol %) exhibited a high UC quantum yield of ~28% in the solvent-less, aerated condition. A steady-state emission spectrum (blue UC emission) similar to that of the normal fluorescence of fluid acceptor was obtained upon exciting the composite with a 532 nm green laser (Fig. 3a,b). In addition, the complete quenching of sensitizer phosphorescence, incident light power dependent UC emission and longer fluorescence decay lifetime of fluid acceptor confirmed TTA-based UC in the D-A composite. A steady quantum efficiency over a longer period under air exposure points to the suppressed diffusion of oxygen molecules into fluid matrix. The molten aliphatic chains attached to the chromophore acted as an effective sealing to prevent susceptibility of UC luminescence to oxygen (Fig. 3c). The exciting result of TTA assisted UC in the aerated condition will definitely make an impact on photon upconversion related area.

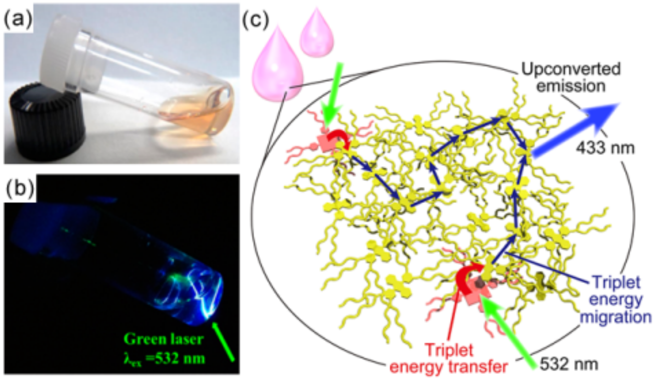

Fig. 3 Photographs of the D-A fluid composite under (a) white light and (b) 532 nm green laser. (c) Schematic illustration of the photon upconversion in the solvent-less ambient atmosphere. Adapted with permission from ref. 11. Copyright 2013 American Chemical Society.

The energy/electron transfer between D-A molecules is always an excellent choice of research due to its vibrant features. But solvent and solvent polarity, presence of molecular oxygen etc. always play a critical fate-determining role. Hence many crucial parameters have to be considered while molecular design. Adachi et al. have reported an efficient room temperature solvent-less energy transfer D-A composite of fluid oligo(*p*-phenyleneethylene) (OPE) derivative and solid fullerene (C_{60}).[12] The π-surface of OPE assisted efficient dispersion of C_{60} which is sparingly soluble in most of the organic solvents. The emission of OPE has been heavily quenched by incorporation of C_{60} due to efficient energy transfer from OPE to C_{60} in the solvent-less condition. Another

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report on fluid porphyrins also proved the feasible dispersion of C_{60} and/or CNTs through efficient D-A interaction, leading to charge transfer.[13] Such D-A composites offer solvent-less “green” energy/electron transfer systems.

Another noticeable development has been observed in the area of photoisomerisation of solvent-less fluid azobenzene to store solar photon energy. In this system, light energy is converted to the chemical bond energy of metastable photoisomers and on applying external stimuli such as heat, voltage or photoirradiation, the stored energy can be discharged on demand as heat. A potential molecular solar thermal energy storage material based on solvent-less azobenzene has opened the door to fluid solar thermal fuels.[14] Morikawa and Kimizuka et al. excelled in storage of photon energy as molecular strain energy in photochemically generated high-energy metastable *cis*-isomer of a solvent-less fluid azobenzene derivative and the stored energy was released as heat by subsequent *cis*-to-*trans* thermal isomerisation. The facile *trans*-to-*cis* and *cis*-to-*trans* photoisomerisation in the neat could avoid the decrease in the net energy density by dilution and hence it can act as a potential solar thermal fuel. The heat released by thermal *cis*-to-*trans* isomerisation has a linear dependence on the *cis* fraction and 100% *cis* isomer exhibited ΔH value of 52 kJ mol^{-1} (47 W h kg^{-1}) (Fig. 4a,b). The clear difference in the absorption intensities of the *trans*- and *cis*-azobenzene under photoirradiation process could be visualised by noticeable color changes (Fig. 4c).

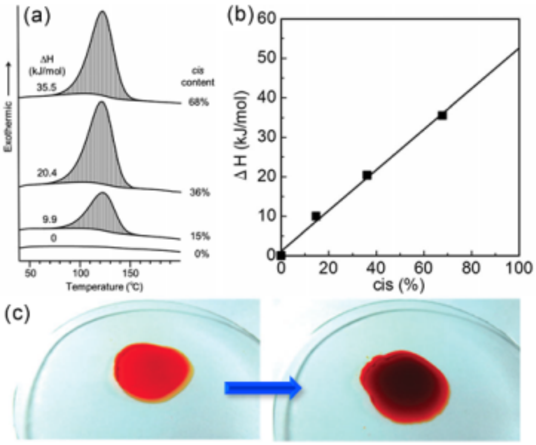

Fig. 4 (a) DSC thermograms of fluid azobenzene at varied molar ratio of the *cis*-isomer. (b) Dependence of *cis*-to-*trans* isomerization enthalpy (ΔH) against the percentage of the *cis*-isomer. (c) Photographs of fluid azobenzene in the discharged state and the charged state. Adapted with permission from ref. 14. Copyright 2014 The Royal Society of Chemistry.

The photochemically reversible liquefaction and solidification of a compound under isothermal conditions has been considered as impractical until Akiyama and co-workers reported the same for an sugar-azo derivative.[15] A sugar alcohol scaffold appended with multi azo-arms exhibited a solid to liquid transition in the neat upon shining with UV light at room temperature. The visible colour of the solid compound gradually changed from yellow to orange upon UV light irradiation and the reverse colour transition occurred under visible light for 10 min. After 1 hour of UV light irradiation, the *trans*-to-*cis* isomerisation of the azobenzene arms resulted in the transition of solid pieces to fluid droplets. Thus obtained fluid was stable for half a day in the dark at room temperature, gradually turned turbid and after 2 days it has been completely transformed to a solid. The liquefaction property has been successfully utilised in the form of photochemically reusable adhesive for photo attaching and detaching of quartz plates at room temperature.

Organic light emitting diode (OLED) displays generated much impact as potential candidates for future lighting displays because of its advantages over conventional counterparts.[16-19] Most importantly, OLEDs could play a significant role in reducing global energy consumption. As a practical demonstration of emissive fluids, a refreshable OLED has been developed using a fluid pyrene emitter by Adachi and coworkers.[20] An LED was designed with a mesh-like cathode and a fluid reservoir in the back side of the cathode (Fig. 5a,b). A decrease in the luminescence efficiency of the device has occurred due to decomposition of the fluid emitter. But the replacement of decomposed molecules with fresh emitters through the mesh cathode resulted in quick emission recovery. The lifetime of such a device could be improved by adding guest molecules into the fluid emitting matrix.[21]

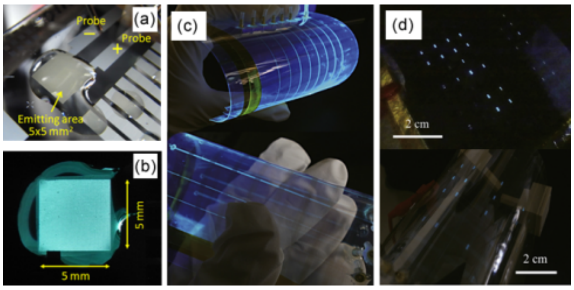

Fig. 5 Photographs of the fluid pyrene based OLED (a) top, (b) bottom views and microfluidic OLED under (c) 365 nm UV light, (d) electroluminescence demonstration with bias in flat (top) and curved (bottom) states. Adapted with permission (a), (b) from ref. 20. Copyright 2012 American Institute of Physics Publishing and (c), (d) from ref. 22. Copyright 2013 Elsevier.

In addition, Mizuno et al. have developed microfluidic flexible and large-area LEDs using fluid pyrene emitter (Fig. 5c,d).[22,23] Here flexible, crack-free light-emitting layer was obtained by using a fluid emitter instead of a solid state emitter. The fluid emitter was continuously injected into the microchannels consisting of ITO anode and cathode pairs, which prevents performance degradation of the device. As shown in Fig. 5c, the fluid emitter flowing through microchannels showed luminescence under UV irradiation. The radiative recombination of electron-hole pairs in the fluid emitter generated electroluminescence under static condition on applying a DC voltage without photo-excitation (Fig. 5d). These demonstrations avoid techniques such as sequential vacuum evaporation through shadow mask and depositing on

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flexible polymer films to prepare emission layers. In order to solve the fundamental problems of luminance, driving-voltage and lifetime associated with fluid OLEDs, more focused research need to be carried out in this direction. Such trails will lead to future large area cost effective and efficient lighting devices with enhanced lifetime.

Besides the above-mentioned examples, there have been many manifestations of solvent-less fluids with promising features.[2] For instance, Nakanishi et al. have reported the pioneering work of solvent-less C_{60} fluids.[24-26] The versatile matrix feature and tunable photoconductivity placed C_{60} fluids as an exceptional candidate. These examples in different contexts of solvent-less fluids also testify the challenges that a relatively new topic put forward.

Conclusions

In the case of solvent assisted systems, energy/electron transfer, photon upconversion, reversible dioxygen binding, and all other related excited and ground state physical parameters are controlled by type of solvent and/or its polarity, presence of oxygen etc. The available fluid matrix in solvent-less systems is highly significant in making the system competitive with the solvent assisted systems. In this manner, the new phase of functional fluids challenges the established paradigms. Solvent-less fluids act as matrices for several organic and inorganic dopants and thus resulted composites may find applications in the future electronic devices. Moreover, the very recent developments of fluid emitter based LEDs also point to a bright future for solvent-less fluids. Hence it is anticipated that the above promising results will open up exciting fields of research and will remain as an inspiration for the realisation of new functional soft materials.

However, solvent-less fluids have limitations including i) loss of charge transport properties due to core isolation, ii) stickiness of the layer surface and iii) least possibility of curability of the final films. In order to overcome these, detailed understanding is needed, especially, in delivering energetically matching donor-acceptor based supramolecular liquids, fluid composites with polymerizable chains, self-healing and curable motives etc. A sensible molecular design strategy and dedicated approach will definitely lead this topic from a lab to market supply of flexible and/or foldable large area energy conversion as well as lighting devices.

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