ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Paul, K. Gayen, N. Nandi and A. Banerjee, *Chem. Commun.*, 2018, DOI: 10.1039/C7CC09824C.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/C7CC09824C

Journal Name

COMMUNICATION

Carbon nano-dots induced gelation of a histidine based amphiphile: Application as a fluorescent Ink and modulation of Gel stiffness

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Subir Paul, Kousik Gayen, Nibedita Nandi and Arindam Banerjee*[,a]

This is a unique example of fluorescent carbon dot induced hydrogelation of an amino acid based amphiphile.Carbon dots to amphiphile ratio dictates the gel stifness. Moreover, this hydrogel can be used as a prominant fluorescent ink and the dried gel shows a remarkable, unusual green fluorescence in the solid state.

Carbon dots(C-dots)[1]is an emerging field in scientific research from the time of their discovery due to the intrinsic fluorescence, photo-stability, chemical robustness, low toxicity, and biocompatibility.[2] This makes them very useful candidate for widespread applications in bioimaging,[3] drug delivery,[4] photoelectronics,[5]photocatalysis[6] and others.[7]Since its discovery, carbon dots has become a good replacement for semiconducting metal oxide, metal chalcogenides quantum dots since the former does not suffer from intrinsic cytotoxicity.[8]One of the major drawbacks of C-dots is that they do not show significant fluorescence in solid state due to aggregation induced quenching phenomenon[9], except a few rare examples.[10] Solid state fluorescence is important and it is highly demanding due to various applications of fluorescent solid materials inlight emitting diodes (LEDs) and security printing.[11] So, it is important to discover fruitful strategies to preserve the fluorescence of C-dots in the solid state. Supramolecular gels[12] derived from assembly of small molecules are a fascinating class of soft materials due to their diversified applications including drug delivery, tissue engineering, catalysis, wound dressing, pollutant removal and others.[13] Two-component hydrogels[14] consisting of two different components provide the opportunity to regulate the gelation property by varying one of the components or both components. It is important to modulate the mechanical stiffness of gels for the growth and development of smart materials. Incorporation of different nanomaterials including metal nano-cluster,[15] metal nanoparticle, graphene oxide,[16]carbon nanotube,[17]C-dots[18]into the gel matrix has been achieved and studied extensively so far. Though there are several examples of modulating gel properties by including nanomaterials into gel matrix, however, in most of the cases the nanomaterials do not play any part in gelation process and the gel network acts as a mere host for the nanomaterials. To the best of our knowledge, there is no systematic studies of C-dots induced two component hydrogelation of an amino acid based amphiphile with tuneable mechanical strength and fluorescence behaviour. A new type of two-component gel has been constructed in such a way that the carboxylic acid functionalities on the carbon dot can interact with the cationic amphiphile to form a hydrogel. This hydrogel exhibits a strong cyan fluorescence, while the xerogel obtained from the hydrogel exhibits green fluorescence in solid state providing a meaningful strategy to overcome the aggregation induced quenching of fluorescence in C-dots. This type of solid state fluorescence is quite unusual for C-dots containing materials reported so far.[11b]The retaining of fluorescence in the solid state facilitates the potential use of this C-dots induced hydrogel as a new type of fluorescent ink for various information storage applications.

C-dots were synthesized via simple hydrothermal treatment of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Ina typical experiment, 200 mg of DDQ was dissolved in 60 ml of Milli-Q water and the solution was placed in a 100 ml teflon lined autoclave followed by heating at 180º C for 3 hours (Fig. S7, ESI†). The resulting brown coloured solution was then centrifuged to separate larger particles and then it was subjected to dialysis for further purification.

The FEG-TEM image of C-dots(Fig. 2a) shows that these C-dots are less than 1 nm in size and show almost monodispersed nature withan average particle size of 0.8 nm. Close inspection reveals no crystallinity among these nanoparticles confirming their amorphous nature and this coincides with the previously reported carbon nanoparticles with such small sizes.[19]

---

[a] *Department of Biological Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032 (India) Fax: (+ 91) 33-2473-2805, E-mail: bcab@iacs.res.in.*

Electronic Supplementary Information (ESI) available: [Experimental section, Instrumentation, Synthetic procedures, NMR, HRMS, Spectroscopic studies, FTIR, Rheological studies.] See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7CC09824C

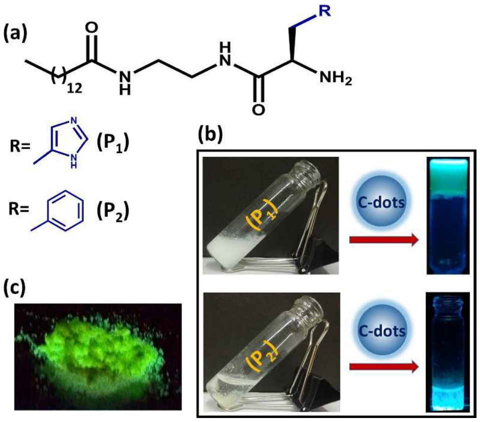


Fig. 1 (a) Chemical structures of amphiphiles**P1**and **P2**. (b) Appearance of the hydrogel and soluble aggregate obtained from **P1** and **P2**respectively on treatment with C-dots (derived fromDDQ) under UV light by irradiating at 365nm. (c) Appearance of the xerogelfrom **P2** hydrogel under UV light.

The FT-IR spectra of C-dots show abundance of different functional groups on the surface of these carbon dots (Fig. S8, ESI†). Broad peaks at 3380 cm-^{1} and 3213 cm^{-1} are assigned to O-H and N-H stretching vibrations. Peaks at 3033 cm^{-1}, 2812 cm^{-1} and 2234 cm^{-1} arise due to =C-H, -C-H and C≡N stretching vibrations. Peaks at 1715 cm^{-1} and 1622 cm^{-1} are assigned to C=O and C=C stretching vibrations and the peaks at 1404 cm^{-1}, 1204 cm^{-1} and 1057 cm^{-1} are assigned as O-H deformation peak, C-OH stretching peak and C-O stretching peaks respectively.[20]

At first we tested the gelation ability of the amphiphile **P1** in Milli-Q water (pH 6.6). In a typical procedure, 4 mg of P1 was taken in a glass vial and it was dissolved in 1 ml water through heating on a hot plate, the vial was then allowed to cool down. As the system attained room temperature only a white coloured dispersion was obtained and no gelation was found. Thus the amphiphile itself does not have any gelation efficiency in water. In another attempt we dissolved 4 mg of **P1** in 800 µl of water by heating and then 200 µl of C-dots solution (containing 1.0 mg of C-dots) was added to the hot amphiphile solution. As the mixture attained room temperature, a brown coloured self-supportive hydrogel was obtained (checked by vial inversion). Different compositions of amino acid based amphiphile **P1** and C-dots were taken to obtain two component gels. Amphiphile to C-dots ratio was varied from 1:1 to 8:1 to obtain a stable two component gel. Outside this range of ratio limit, no gelation was observed. We were curios to find out the driving force behind this gelation phenomenon as the amphiphile could only form a gel in water in the presence of carbon dots. As the surface of the carbon dots is highly functionalized with different functional groups, we envisaged that the interaction of the amphiphile with some particular functionalities of the carbon dots surface must be the driving force behind gelation. To investigate this hypothesis, we tested for the probable gelation ability of the amphiphile with common organic molecules bearing –COOH, -OH and –NH$_2$ functionalities. For this purpose trimesic acid, Tris(2-aminoethyl)amine(TREN) and catechol were used. We observed that the amphiphile formed self-supportive two-component hydrogel with trimesic acid. However, in presence of TREN or catechol no gelation was observed (Fig. S9, ESI†) under similar conditions and other tested conditions. This observation is pretty instructive and points towards the interaction between –COOH groups of C-dots and the amphiphile for playing a crucial role in gelation. Moreover, a strong interaction between the imidazole ring of histidine and the carboxylic group also plays an important role.[21]To probe the importance of the imidazole ring of the histidine moiety, another amphiphile **P2** (Fig. 1) has been designed and synthesised by replacing the –His residue with a –Phe residue. It is observed that the amphiphile **P2** does not form any hydrogel under similar and widely tested conditions. These findings clearly suggest that the interaction between the imidazole ring of histidine and the –COOH groups on carbon dots is the driving force for this two component gelation.

To get insight into the morphological behaviour of the amphiphile aggregate and the amphiphile-C dots gel, field-emission scanning electron microscopy (FE-SEM) and field-emission transmission electron microscopy (FEG-TEM) experiments were carried out. From the FE-SEM images (Fig. S10, ESI†),it is clear that the two-component hydrogel is composed of a much dense fibrillar network than that of the aggregated moiety. FEG-TEM image of the gel shows the presence of entangled fibres of width ranging from 16 to 25 nm. The FEG-TEM image (Fig. 2c) of the carbon dots inside the gel matrix was found to be quite different from the FEG-TEM images of as-prepared C-dots (Fig-2a). It is apparent from the image that the size of the C-dots within the gel varies between 4.5 to 6 nm with an average size of 5 nm (Fig. 2d). This is in sharp contrast to the results obtained from the as-prepared C-dots with the average size of 0.8 nm (Fig. 2b). We envisioned that within the self-assembled gel medium carbon dots also undergo some aggregation and it results in bigger particle sizes as it is evident from FEG-TEM images of C-dots in gel (Fig. 2d). This aggregation of C-dots upon gelation may be responsible for the red shift of the fluorescence of the carbon dots in the gel matrix compared to the fluorescence of the as-prepared C-dots (Fig 3).

The visco-elastic property of these hydrogels has been measured using frequency sweep experiments. It is observed from the Fig. 2f that the storage modulus (G′) value is the lowest for the two-component gel containing amhiphile to C-dots ratio4:1 and it increases with an increase in the C-dots proportion in the gel matrix. It is found that at an angular frequency of 0.72 rad/s, for 4:1 (w/w) gel, G′ value is 1.9 × 10^{3}Pa, for 2:1 (w/w) gel it is 2.9 × 10^{3}Pa and for 1:1 (w/w)gel it is 5.0 × 10^{3}Pa. So, there is an increase of 69.23% in G′ value as we move from 4:1 (w/w) to 2:1 (w/w) gel and an increase in 56.93% in G′ value is noticed as we move from 2:1 (w/w) gel to 1:1 (w/w) gel. So, it can be said that the mechanical strength of the gel can be easily tuned by varying the amount of C-dots in the gel matrix.

As the gel was broken upon mechanical shaking and then reformed upon resting (Fig. S11, ESI†), time dependent step-strain experiment was performed to investigate its mechano-

View Article Online
DOI: 10.1039/C7CC09824C

responsive nature. A 2 ml gel containing 8 mg of amphiphile and 4 mg of carbon dots was used for the time dependent step strain experiment (Fig. S12, ESI†).At first a low strain of 0.1% was applied for 100 seconds and the values of G’ and G” were measured. The G’ value was found to be higher than the G” value under this strain indicating the gel nature. Then the strain was increased to 100% at once and this strain was maintained for the next 100 seconds. Under this increased strain the G’ attained a lower value than G” indicating the transformation of the gel to sol. To allow the gel to reform, the strain was again reduced to 0.1 % and it was kept at that value for next hundred seconds. The values of G’ and G” were increased and regained their initial values after 70 seconds.

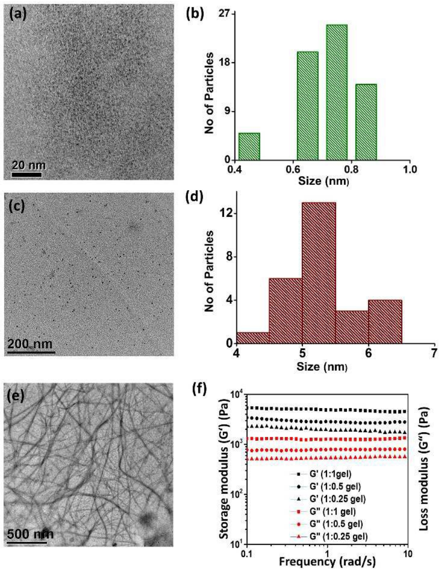


Fig. 2 (a) FEG-TEM image and (b) size distribution of as prepared C-dots. (c) FEG-TEM image and (d) size distribution of C-dots in gel. (e) FEG-TEM image shows nanofibrilar network assembly of C-dots gel. (f) Frequency sweep data showing increase in gel strength with increase in C-dots proportion in the gel matrix.

The C-dots are soluble in polar solvents like water, DMF, DMSO and methanol and in water they show bright cyan fluorescence upon irradiation with 365 nm illumination of a hand-held UV lamp. Fig.3a shows fluorescence spectra of the as-prepared C-dots at various excitation wavelengths. It is apparent from this figure that the emission peak is centred at 446 nm showing no change of emission by the variation of the excitation wavelength from 345 nm to 415 nm. However, there is a change in intensity of emission spectra by increasing the excitation wavelength upto 385 nm and then it starts decreasing slightly upto 415 nm. So it can be said that these carbon dots show excitation independent emission in aqueous medium and this is rare.[22]The UV-visible spectra of as-prepared C-dots (Fig. S13, ESI†) illustrates a small peak at 294 nm corresponding to the π-πtransition in the carbogenic core, while the peak at 388 nm with a shoulder at 385 nm can arise due to the n- π transition of C=O and C=N[23]. The two-component hydrogel containing the C-dots and the amino acid based amphiphile shows a green emission upon the irradiation of 365 nm by a UV lamp. Fig. 3a shows the excitation dependent emission spectra of the hydrogel. It is apparent from Fig. 3athat there is a slight red shift of 5 nm as the excitation wavelength is increased from 345 to 405 nm and it is accompanied by a steady increase in the emission intensity as the excitation wavelength is increased from 345 to 385 nm. Thereafter, it drops slightly for the excitation at 405 nm. So, it can be stated that at excitation of 385 nm, the maximum emission is observed for the as-prepared C-dots and C-dots containing gel. In C-dots containing gel the emission is 25 nm red shifted compared to that of the as prepared C-dots solution in water. New surface states may be been incorporated upon interaction of histidine and carbon dots surface[24] during gelation and this leads to the red shift of the carbon dots fluorescence. The carbon dots containing gel with a composition of amphiphile to C-dots ratio of 8:1 (w/w) was freeze dried to obtain the xerogel and this was subjected to solid state fluorescence study. This xerogel emits a bright bluish green fluorescence upon the irradiation at 365 nm by illuminating through a hand held UV lamp (Fig. 1c). In Fig. 3c shows the emission peak of the xerogel materials at different excitation wavelengths. It is evident from the Fig. 3c that the xerogel too exhibits excitation independent fluorescence peak at 393 nm and it can be stated that this emission peak is 20 nm red shifted from the emission of the C-dots containing hydrogel. The fluorescence quantum yield of the xerogel (in the solid state) is found to be 13%. Generally, the fluorescence of the C-dots is quenched at solid state. However, in this study we got a very bright and significant florescence that has emerged from the xerogel. No fluorescence is observed from the xerogel when the composition of C-dots to amphiphile ratio is more than 1:2 (w/w).For achieving fluorescent xerogel the highest loading fraction of carbon dots is found to be 33.33 (% w/w). This is quite high compared to the previously reported materials[11a] and thus it is an efficient system for conserving the fluorescence of carbon dots in its solid state.

C-dots have been extensively used as fluorescent inks.[25]For an ideal fluorescent ink application, it is desirable that the fluorescent species should show solid state fluorescence.[11b] However, it is not the case for most of the carbon dots reported so far as they suffer from aggregation induced fluorescent quenching in the solid state. When the ink is dried, there is every possibility that the ink will lose its fluorescence (Fig. 3d) rendering it unsuitable for practical application. In our system, the fluorescence of the carbon dots is effectively conserved in the solid state. So, this two-component hydrogel system can be used effectively as a fluorescent ink. Fig. 3ddemonstrates the writings with the carbon dots solution in water fluoresce initially, after the evaporation of water with time the fluorescence of the carbon dots disappears due to aggregation induced quenching. So, the writings are no longer visible. Interestingly, the writings with the gel remain fluorescent even after the evaporation of water molecules with time. This indicates the important application of this material as a fluorescent ink in future.

This study convincingly demonstrates C-dots induced gelation of a histidine based amphiphile through non-covalent interactions in water medium. Mechanical strength of this two

View Article Online
DOI: 10.1039/C7CC09824C

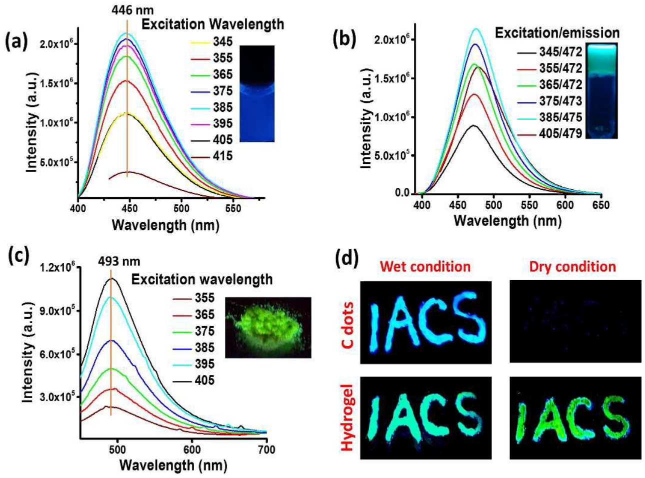


Fig. 3 Fluorescence spectra of (a) as prepared C-dots in water (0.1 (b) C-dots hydrogel (c) xerogel obtained from hydrogel. (inset shows corresponding optical images under UV illumination of 365 nm) (d) Fluorescentink application of C-dots gel showing its superiority to as prepared c-dots.

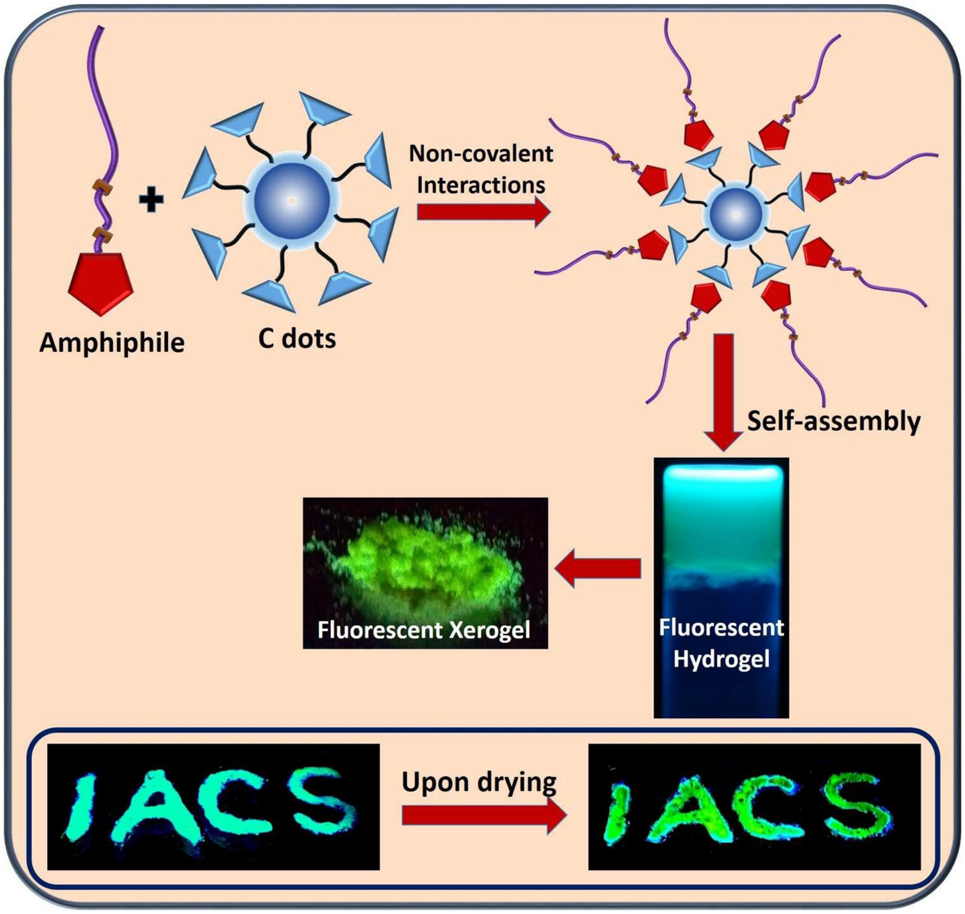
component gel has been successfully tuned by varying the ratio of C-dots to amphiphile. The hydrogel shows a remarkable cyan fluorescence, while the xerogel shows a green fluorescence. This gel based soft material has been utilized as a good fluorescent ink on the glass plate and it is visible under UV light even after the evaporation of water molecules, as the dried gel is also fluorescent. This holds the future promise for using this material in device applications.

S. P, K. G and N. N. gratefully acknowledge CSIR and DST, New Delhi, India for financial assistance. We also sincerely acknowledge Mr. K. S. Das for carrying the rheological experiments and Mr. S. Mandal for measuring the solid state fluorescence quantum yield.

Notes and References

1 Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S.-Y. Xie, *J. Am. Chem. Soc.* 2006, **128**, 7756-7757.
2 (a) X. Li, M. Rui, J. Song, Z.Shen and H. Zeng, *Adv. Funct. Mater.,* 2015, **25**, 4929–4947. (b) S. N. Baker and G. A. Baker, *Angew. Chem. Int. Ed.* 2010, **49**, 6726 – 6744.
3 (a) J. Zhang and S. –H. Yu, *Mater. Today*, 2016, **19**, 382-393. (b) L. Li, C. Lu, S. Li, S. Liu, L. Wang, W. Cai, W. Xu, X. Yang, Y. Liu and R. Zhang, *J. Mater. Chem. B*, 2017, **5**, 1935–1942.
4 Q. Zeng, D. Shao, X. He, Z. Ren, W. Ji, C. Shan, S. Qu, J. Li, L.Chen and Q. Li, *J. Mater. Chem. B*, 2016, **4**, 5119–5126.
5 J. B. Essner and G. A. Baker, *Environ. Sci. Nano*, 2017, **4**, 1216–1263.
6 Z. Zhang, T.Zheng, X. Li, J. Xu and H. Zeng, *Part. Part. Syst. Charact.*, 2016, **33**, 457–472.
7 Y. Wang and A. Hu, *J. Mater. Chem. C*, 2014, **2**, 6921-6939.
8 S. Y. Lim, W.Shen and Z.Gao, *Chem. Soc. Rev.*, 2015,**44**, 362-381.
9 Z.-S. Qian, L.-J. Chai, Y.-Y. Huang, C. Tang, J.-J. Shen, J.-R. Chen, H. Feng, Biosens. Bioelectron., 2015, 68, 675–680.
10 (a) Y. Chen, M. Zheng, Y. Xiao, H. Dong, H. Zhang, J. Zhuang, H. Hu, B. Lei and Y. Liu, *c. Mater.*, 2016, **28**, 312–318. (b)J. He, Y. He, Y. Chen, B. Lei, J. Zhuang, Y. Xiao, Y. Liang, M. Zheng, H. Zhang and Y. Liu, *Small*, 2017, **13**, 1–10.
11 (a) D. Zhou, D. Li, P. Jing, Y. Zhai, D. Shen, S. Qu and A. L. Rogach, *Chem. Mater.*, 2017, **29**, 1779–1787. (b) X. Hou, C. Ke, C. J. Bruns, P. R. McGonigal, R. B. Pettman and J. F. Stoddart, *Nat. Commun.*, 2015, **6**, 1–9.
12 (a) J. Li, X. Du, S. Hashim, A. Shy and B. Xu, *J. Am. Chem. Soc.*, 2017, **139**, 71–74. (b) K. Lalitha, Y. S. Prasad, V. Sridharan, C. U. Maheswari, G. John and S. Nagarajan, *RSC Adv.*, 2015, **5**, 77589–77594.
13 (a) H. Vilaça, T. Castro, F. M. G. Costa, M. Melle-Franco, L. Hilliou, I. W. Hamley, E. M. S. Castanheira, J. A. Martins and P. M. T. Ferreira, *J. Mater. Chem. B*, 2017, **5**, 8607–8617. (b)J. E. P. Sun, B. Stewart, A. Litan, S. J. Lee, J. P. Schneider, S. A. Langhans and D. J. Pochan, *Biomater. Sci.*, 2016, **4**, 839–848.(c) T. N. Vo, S. R. Shah, S. Lu, A. M. Tatara, E. J. Lee, T. T. Roh, Y. Tabata and A. G. Mikos, *Biomaterials*, 2016, **83**, 1–11. (d)J. Nanda, A. Biswas, B. Adhikari and A. Banerjee, *Angew. Chem. Int. Ed.*, 2013, **52**, 5041–5045. (e) F. Rodríguez-Llansola, J. F. Miravet and B. Escuder, *Chem. Commun.*, 2009, 7303-7305. (f) M. D. Konieczynska, J. C. Villa-Camacho, C. Ghobril, M. Perez-Viloria, K. M. Tevis, W. A. Blessing, A. Nazarian, E. K. Rodriguez and M. W. Grinstaff, *Angew. Chem. Int. Ed.*, 2016, **55**, 9984–9987. (g)B. O. Okesola and D. K. Smith, *Chem. Soc. Rev.*, 2016, **45**, 4226–4251. (h) N. Nandi, A. Baral, K. Basu, S. Roy and A. Banerjee, *Pept. Sci.,*2017, 108:e22915. (i) P. K. Vemula, N. Wiradharma, J. A. Ankrum, O. R. Miranda, G. John and J. M. Karp, *Curr. Opin. Biotechnol.,* 2013, **24**, 1174–1182. (j) K. P. Divya, M. Miroshnikov, D. Dutta, P. K. Vemula, P. M. Ajayan and G. John, *Acc. Che. Res.*, 2016, **49**, 1671-1680.
14 (a) Y. M. Abul-Haija, G. Scott, J. K. Sahoo, T. Tuttle and R. Ulijn, *Chem. Commun.*, 2017, **53**, 9562–9565. (b) V. M. P. Vieira, L. L. Hay and D. K. Smith, *Chem. Sci.*, 2017, **8**, 6981–6990. (c) E. R. Draper, M. Wallace, R. Schweins, R. J. Poole and D. J. Adams, *Langmuir*, 2017, **33**, 2387–2395.
15 S. Roy and A. Banerjee, *Soft Matter*, 2011, **7**, 5300-5308.
16 A. Biswas and A. Banerjee, *Soft Matter*, 2015, **11**, 4226–4234.
17 S. Ahadian, J. Ramón-Azcón, M. Estili, X. Liang, S. Ostrovidov, H. Shiku, M. Ramalingam, K. Nakajima, Y. Sakka, H. Bae, T. Matsue and A. Khademhosseini, *Sci. Rep.*, 2014, **4**, 1–11.
18 (a) A. Cayuela, S. R. Kennedy, M. L. Soriano, C. D. Jones, M. Valcárcel and J. W. Steed, *Chem. Sci.*, 2015, **6**, 6139–6146.
(b*)*S. Bhattacharya, S. Nandi, R. Jelinek,*RSC Adv.*, 2017, **7**, 588-594.
19 V. Strauss, J. T. Margraf, C. Dolle, B. Butz, T. J. Nacken, W. Bauer, W. Peukert, E. Spiecker, T. Clark and D. M. Guldi, *J. Am. Chem. Soc.,* 2014, **136**, 17308−17316.
20 J.-L. Chen and X.-P. Yan, *Chem. Commun.*, 2011, **47**, 3135-3137.
21 (a) J. Chen, T. Wang and M. Liu, *Chem. Commun.*, 2016, **52**, 6123–6126. (b) Y. Liu, C. Chen, T. Wang and M. Liu, *Langmuir*, 2016, **32**, 322–328. (c) C. Chen, T. Wang, Y. Fu and M. Liu, *Chem. Commun.*, 2016, **52**, 1381–1384.
22 D. Chen, H.Gao, X. Chen, G. Fang, S. Yuan and Y. Yuan, *ACS Photonics,* 2017, **4**, 2352−2358.
23 J. Hou, L. Wang, P. Zhang, Y. Xu and L. Ding, *Chem. Commun.*, 2015, **51**, 17768–17771.
24 S. D. Choudhury, J. M. Chethodil, P. M. Gharat, P. K. Praseetha and H. Pal, , *Chem. Commun.*, 2015, **51**, 17768—17771.
25 (a)S. Qu, X. Wang, Q. Lu, X. Liu and L. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 12215–12218. (b) L. Zhu, Y. Yin, C-F Wang, S. Chen,*J. Mater. Chem.* C, 2013, **1**, 4925. (c) J. Shen, Q. Li, Y. Zhang, X-j She, C.-F. Wanga and S. Chen*RSC Adv.*, 2016, **6**, 59702.

View Article Online
DOI: 10.1039/C7CC09824C



324x311mm (150 x 150 DPI)