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## BODIPY Based Self-healing Fluorescent Gel Formation via Acylhydrazone Linkage

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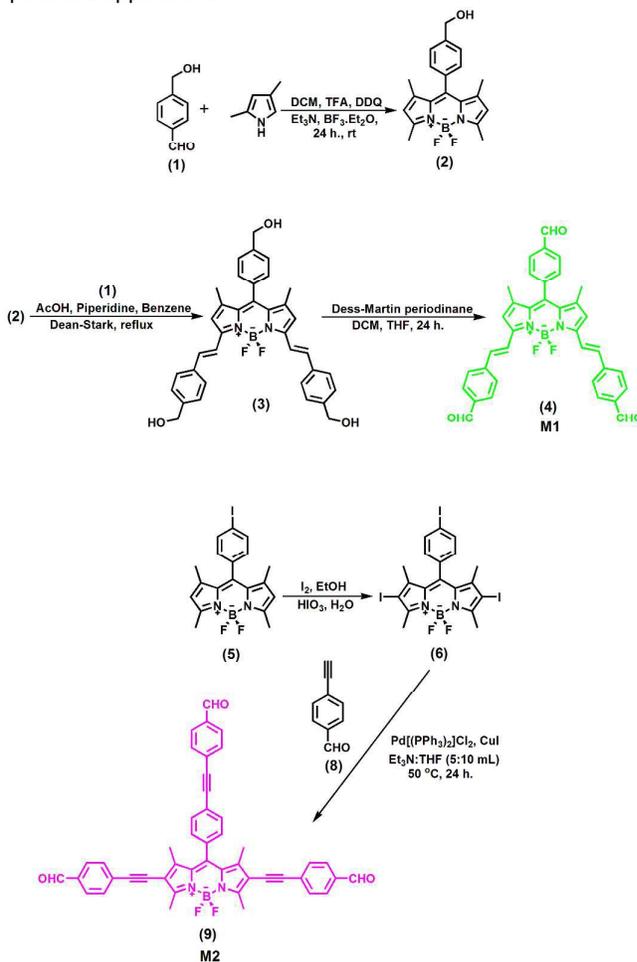
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**Polymeric BODIPY derivatives with reactive functional groups undergo reversible formation of covalent bonds leading to self-healing properties. Cross-reactivity of acyl-hydrazine and aldehyde moieties forms the basis of dynamic covalent chemistry leading to sol-gel transition in this series of compounds. In addition, thin layers of absorbers show efficient energy transfer indicating a potential in solar concentration.**

Self-healing is a very intriguing emergent property which was until recently kept in the domain of biological systems.<sup>1-8</sup> Reversible supramolecular interactions and certain covalent transformations which are also reversible under ambient conditions provided an avenue for the realization of self-healing with non-biological smart materials.<sup>9-18</sup> Having the potential to repair the damage caused by mechanical use over time, these polymeric materials are, and will be highly sought-after in considerations for safety, extended use period and energy conservation.<sup>19-24</sup> In general, tiny fractures or defects on the surface of the polymeric materials are difficult to correct, but self-healing property offers a great advantage in this regard, extending the functional use period significantly.<sup>25</sup> Judiciously engineered covalent inter-actions have the potential to result in particularly robust materials with such self-healing capability. Any tear or break in the material will leave behind multiple adhesive/cross-reactive termini, which on contact, would reinstate the covalent bonds ruptured by the physical effector in the first place. Cross-linked covalent polymers with self-healing properties are expected to result in particularly durable materials.<sup>26-35</sup>

During the past decade, the progress made in BODIPY chemistry has attracted considerable attention due to their

high quantum yields, ease of derivatization and a multitude of potential applications.<sup>36-42</sup>



**Scheme 1.** Synthesis of monomers **M1** and **M2**.

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In this study, our goal was to combine the two phenomena namely, through space energy transfer and self-healing ability, to open a new path towards a new generation of solar concentrators. We targeted the synthesis of two gels (**G1** and **G2**), which are to function as energy donor and acceptor layers. To that end, a BODIPY donor monomer **M1** with triformyl groups and a BODIPY acceptor monomer **M2** were separately synthesized.

For the synthesis of **M1**, firstly triiodo-BODIPY derivative (compound **6**) was synthesized and then 4-ethynyl benzaldehyde groups were attached this compound via Sonogashira coupling. The synthesis for the second monomer **M2** started with the reaction of known BODIPY dye (compound **2**) with 4-(hydroxymethyl) benzaldehyde under Knoevenagel conditions (Scheme 1). Thus, the monomer **M2** was designed to have longer absorption and emission wavelenghts, compared to the monomer **M1** due to extended of conjugation and strong intramolecular charge transfer (ICT) (Supplementary Information, Table S1). **M2** was obtained via subsequent formylation with Dess–Martin periodianane. Following that conversion, a bis-acylhydrazine functionalized PEO polymer **P1** (Polyethyleneoxide, Mn=2000) was prepared according to literature.<sup>43</sup> This polymer was used previously in the reversible conversion to poly(acylhydrazone) compounds.

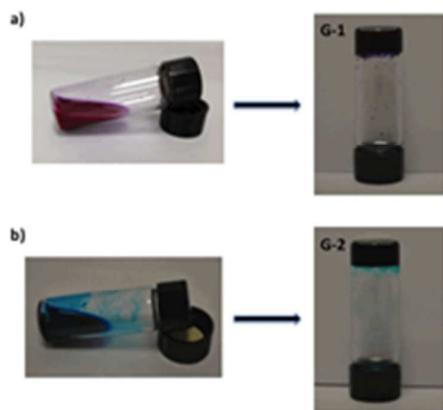


Fig. 1. Inverted vial test demonstration: on acid addition at room temperature, transition to gel state is observed as evidenced by the inverted vial test and gelation was completed about 2 hours under these conditions. On the other hand, gels (**G1** and **G2**) responded to added triethylamine changes showing a reversal to sol phase. The sol-gel transition of fluorescent donor dye (a) and fluorescent acceptor dye (b). The compositions of gels are 0.02 mmol polymer (**P1**), 0.0134 mmol dye (**M1** or **M2**), 30  $\mu$ L acetic acid in 0.4 mL DMF.

Gel formation reaction was carried out in DMF using BODIPY based monomers **M1**, **M2** and the PEO polymer **P1**, and it proceeds by the formation of acylhydrazone linkage. The sol-gel transition of the fluorescent material (Fig. 1) was affected by the addition of acetic acid, as the addition of catalytic amount of acid is known to facilitate this reaction.<sup>44</sup> As expected, on acid addition at room temperature, transition to gel state is observed as evidenced by the inverted vial test

and gelation was completed about 2 hours under these conditions. IR spectra of dried gel formed in dichloromethane (Fig. S18) showed absorption band at 3496  $\text{cm}^{-1}$  due to the presence of -NH group. In addition, the band observed at 1606  $\text{cm}^{-1}$  corresponds to C=N linkage and indicates the formation of acylhydrazone bond.

On the other hand, gels (**G1** and **G2**) responded to added base (triethylamine) changes showing a reversal to sol phase (Supplementary Information, Fig. S2). For the sol gel transition firstly hydrochloric acid (5  $\mu$ L) was added on the gel surface, after waiting 2 hours gel turns into sol due to hydrolysis of acylhydrazone bond at higher acidic conditions, so after adding triethylamine (8  $\mu$ L) to this solution, sol turns into gel because of the formation of acylhydrazone bond again.

Self-healing properties of the gel materials were investigated initially, by bringing together two pieces of the gel and holding them in contact to form a single piece, without any other external influence. Following a brief period, the two pieces were reattached visibly (Fig. 2). In addition, two gel pieces prepared using the polymeric linker and the donor BODIPY monomers, and the acceptor BODIPY monomers were brought together in the same way.

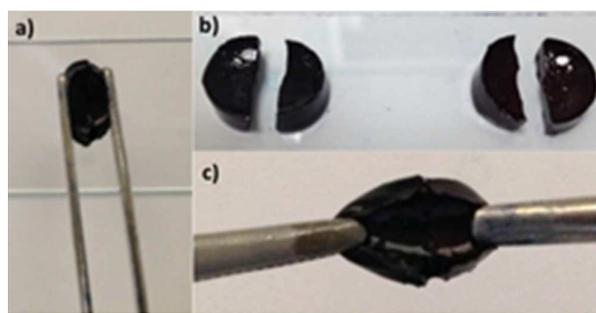


Fig. 2. The digital photographs of the cracked and merged fluorescent donor and acceptor gels: a) merged donor gel (left half) and acceptor gel (right half) by putting donor half and acceptor half together for two hours at ambient temperature, b) cracked donor gel (left) and acceptor gel (right), c) also merged donor gel (left half) and acceptor gel (right half) pulled by tweezers.

Rheological measurements were also carried out in order to determine and compare the strengths of **G1**, **G2** and the healed gel. The rheological spectra of **G1**, **G2** and the healed gel show that storage modulus ( $G'$ ) is much larger than the loss modulus ( $G''$ ) and it does not depend on angular frequency  $\omega$ , suggesting an organogel formation (Fig. 3a-c). In addition,  $G'$  vs  $\omega$  plot shows a wide plateau indication of covalent cross-linked polymer gel.<sup>45</sup> The stress-strain at break of **G1**, **G2** and the self-healed gel which was obtained by bringing together the two pieces of **G1** and **G2** are shown in Fig. 3d. The toughness which is the area under the stress-strain curve is almost same for **G1**, **G2** and the healed gel. Hence the healing efficiency of healed gel is determined as 100% with respect to **G1** and **G2**.<sup>46</sup>

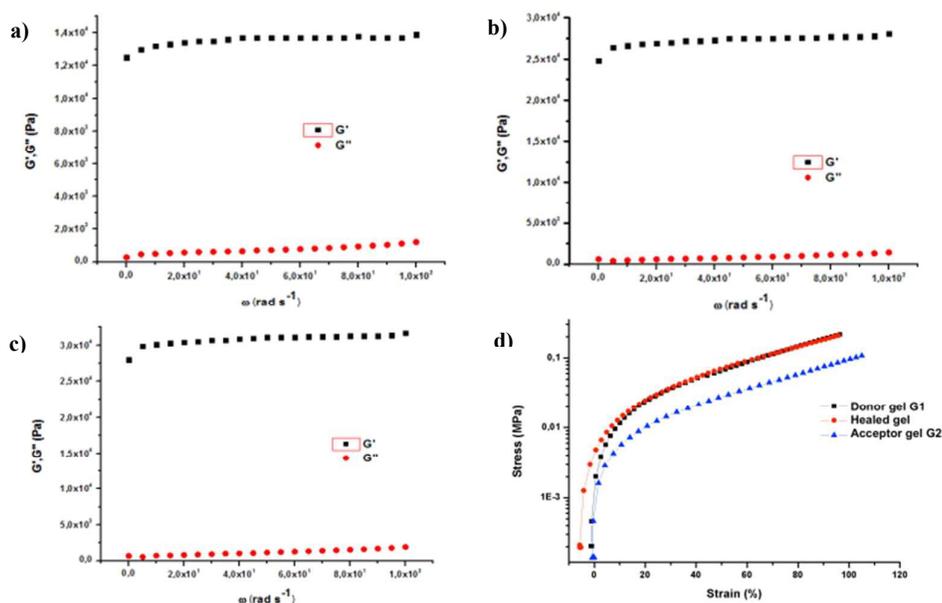


Fig. 3. Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) vs angular frequency ( $\omega$ ) of donor gel (**G1**) (a), acceptor gel (**G2**) (b), and healed gel (c). Stress strain curves of donor gel (**G1**), acceptor gel (**G2**) and healed gel (d)

Healing at the microscopic level was investigated as well, for that purpose **G1**, which consists of donor monomer **M1** and PEO polymer **P1**, was deliberately damaged by a needle tip and microscopy shows the disappearance of the wedge under optical microscope after two hours, and SEM images are also supportive of rebuilding of the surface (Fig. 4).

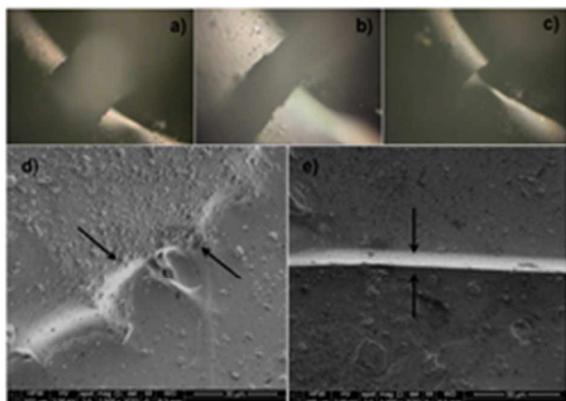


Fig. 4. Optical microscope images of mechanically damaged fluorescent self-healing donor gel (a), after one hour (b) and after two hours (c). SEM images of fluorescent self-healing donor gel show healing line after cutting and healing gel (d) and (e).

To investigate energy transfer properties between donor gel **G1** and acceptor gel **G2**, initially we acquired the photoluminescence spectra of gels directly from the gel phase, **G1** has an emission peak at 605 nm, and **G2** at 658 nm. The normalized emission spectra of the gels are shown in Fig. 5.

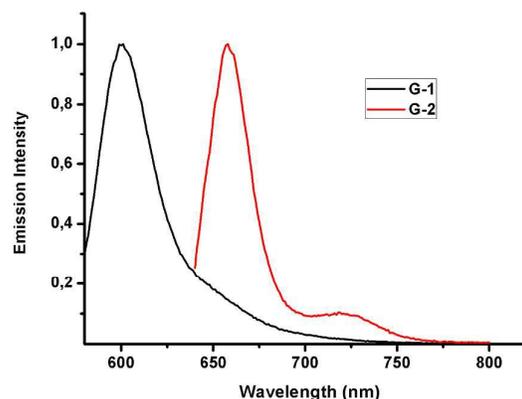


Fig. 5. The emission spectra of fluorescent self-healing donor gel and fluorescent self-healing acceptor gel at 575 nm for donor gel and at 645 nm for acceptor gel. The data were acquired from **G1** and **G2** gel phase separately.

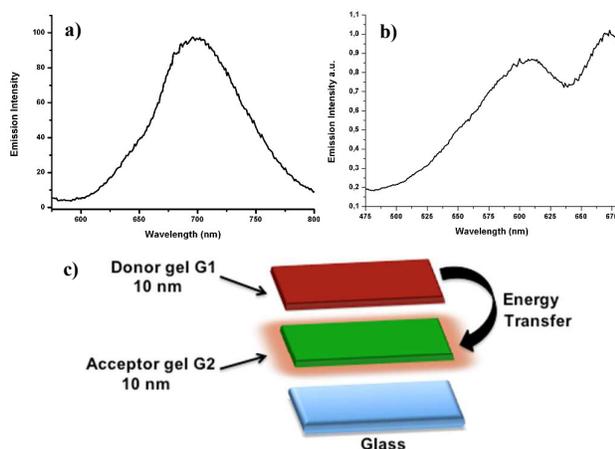


Fig. 6. The emission and excitation spectra for the spin coated (10 nm for **G1** and **G2**, respectively) glass with fluorescent self-healing donor gel **G1** and fluorescent self-healing acceptor gel **G2**. a) The emission spectrum of spin coated glass excited at 550 nm. b) Excitation spectrum of spin coated glass (The emission data were collected at 700 nm). c) Schematic representations of spin coating set-up for fluorescent self-healing donor gel (**G1**, 10 nm thickness, 8000 rpm for one minute) and fluorescent self-healing acceptor gel (**G2**, 10 nm thickness, 8000 rpm for one minute).

Besides the spectral overlap, proximity of the donor-acceptor pair is significant for fluorescence energy transfer phenomenon. So in order to perform energy transfer in gel phase, self-healing ability of gels provide proximity of molecules on contact surfaces of gels (**G1** and **G2**). Hence, a glass surface was coated by spin coating with the solution containing precursors of **G1** at 8000 rpm for one minute. Then it was set aside for the completion of gelation. This coated surface with **G1** was then coated with the other gel **G2** by the same method and the thickness of the both gel layers were determined 10 nm by profilometer (Fig. 6). The excitation spectrum obtained using the two-layers of the gel shows a clear evidence of energy transfer between the fluorescent gel layers (Fig. 6). Here, self-healing takes place between contact surfaces of gels through condensation reaction between acylhydrazine and aldehyde groups in the gels. Thus, the Förster type energy transfer<sup>47</sup> between donor and acceptor gel surfaces occurs because of the formation of dynamic covalent bonds on contacting surfaces of the self-healed donor and acceptor gels.

A plot of energy transfer efficiency (Fig. S16) as a function of wavelength,<sup>48</sup> yields energy transfer efficiencies above 90% in the region of analysis. This means that the energy transfer between the gel layers is promising for potential use in solar concentrator applications.<sup>49</sup> On the other hand, the energy transfer efficiency for the mixture of monomers **M1** and **M2** is determined in sol phase (in chloroform) as about 30% (Fig S17). This result shows that some energy transfer occurs in sol phase because the donor and acceptor modules are closer

each other. However we do not think that it is a nonradiative FRET, it is most probably a valueless radiative energy transfer.

With this work for the first time two fluorescent gel materials, which have self-healing characteristics were synthesized and shown to cascade energy from the shorter wavelength absorbing gel (donor gel **G1**) to the longer wavelength absorbing (acceptor gel **G2**) one. An induced tear in both gels are effectively healed in a relatively short amount of time. We are confident that materials designed with this approach are likely to have a practical potential in luminescent solar concentrators. Our work to that end is in progress.

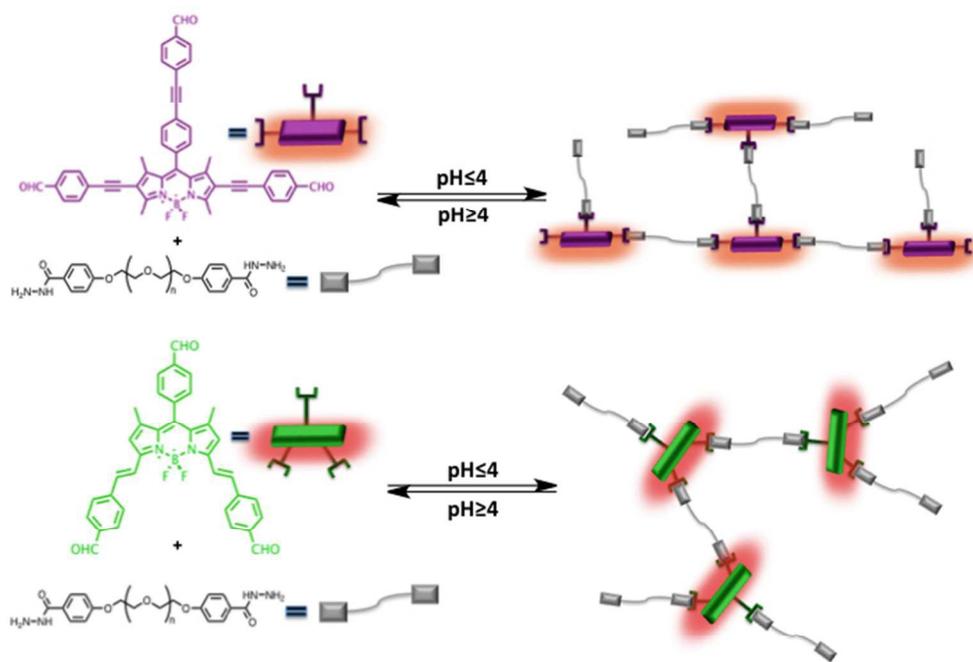
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#### References

- 1 A. Phadke, C. Zhanga, B. Armanb, C.-C. Hsueh, R. A. Mashelkard, A. K. Leled, M. J. Tauberc, G. Aryab and S. Varghesea, *Proc. Natl. Acad. Sci.*, 2012, **109**, 4383.
- 2 K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara and H. Otsuka, *Angew. Chem. Int. Ed.*, 2012, **51**, 1138.
- 3 X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698.
- 4 R. Nicola, J. Kamada, A. V. Wassen and K. Matyjaszewski, *Macromolecules*, 2010, **43**, 4355.
- 5 Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara and K. Matyjaszewski, *Angew. Chem. Int. Ed.* 2011, **50**, 1660.
- 6 E. B. Murphy, E. Bolanos, C. Schaffner-Hamann, F. Wudl, S. R. Nutt and M. L. Auad, *Macromolecules*, 2008, **41**, 5203.
- 7 K. Ishida and N. Yoshie, *Macromol. Biosci.*, 2008, **8**, 916.
- 8 Y. Ruff and J.-M. Lehn, *Angew. Chem. Int. Ed.* 2008, **47**, 3556.
- 9 Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrinyi, P. H. Dussault, Y. Osadag and Y. M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 8114.
- 10 E. Kolomiets and J. M. Lehn, *Chem. Commun.*, 2005, 1519.
- 11 J. M. Lehn, *Prog. Polym. Sci.*, 2005, **30**, 814.
- 12 S. Otto, R. L. Furlan and J. K. Sanders, *DrugDiscoveryToday*, 2002, **7**, 117.
- 13 J. M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151.
- 14 C. R. South, C. Burd and M. Weck, *Acc. Chem. Res.*, 2007, **40**, 63.
- 15 S. J. Rowan, S. J. Cantrill, G. R. Cousins, J. K. Sanders and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2002, **41**, 898.
- 16 S. K. M. Nalluri, C. Berdugo, N. Javid, P. W. J. M. Frederix and R. V. Ulijn, *Angew. Chem., Int. Ed.*, 2014, **53**, 5882.
- 17 S. K. M. Nalluri and R. V. Ulijn, *Chem. Sci.*, 2013, **4**, 3699.
- 18 M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng and F. Huang, *Angew. Chem. Int. Ed.*, 2012, **51**, 7011.
- 19 M. Nakahata, Y. Takashima, H. Yamaguchi and A. Harada, *Nat. Commun.* 2, 511.
- 20 B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos and S. R. White, *Annu. Rev. Mater. Res.*, 2010, **40**, 179.

- 21 Y. Chen, A. M. Kushner, G. A. Williams and Z. Guan, *Nat. Chem.*, 2012, **4**, 467–472.
- 22 *Frontiers of Self-Healing Materials and Applications*, ed. N. Shinya, CMC Publishing Co., 2010.
- 23 *Self-Healing Materials: Fundamental, Design Strategies, and Applications*, ed. S. K. Ghosh, Wiley-VCH, 2009.
- 24 T. Shu, J. Wu, M. Lu, L. Chen, T. Yi, F. Li and C. Huang, *J. Mater. Chem.*, 2008, **18**, 886.
- 25 Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrinyi, P. H. Dussault, Y. Osadag and Y. M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 8114.
- 26 L. B. Cappeletti, E. Moncada, J. Poisson, I. S. Butler and J. H. Z. DosSantos, *Appl. Spectrosc.*, 2013, **67**, 441.
- 27 S. K. Goswami, C. J. McAdam, A. M. Lee, L. R. Hanton and S. C. Moratti, *J. Mater. Chem. A*, 2013, **1**, 3415.
- 28 Y. M. Chen, Z. Q. Liu, Z. H. Feng, F. Xu and J. K. Liu, *J. Biomed. Mater. Res., Part A*, 2013, **102**, 2258.
- 29 A. S. Hoffman, *Adv. Drug Delivery Rev.*, 2012, **65**, 10.
- 30 Y. M. Chen, R. Ogawa, A. Kakugo, Y. Osada and J. P. Gong, *Soft Matter*, 2009, **5**, 1804.
- 31 K. Y. Lee and D. J. Mooney, *Chem. Rev.*, 2001, **101**, 1869.
- 32 G. Y. Huang, L. Wang, S. L. Wang, Y. L. Han, J. Wu, Q. Zhang, F. Xu and T. J. Lu, *Biofabrication*, 2012, **4**, 42001.
- 33 G. Y. Huang, L. H. Zhou, Q. C. Zhang, Y. M. Chen, W. Sun, F. Xu and T. J. Lu, *Biofabrication*, 2011, **3**, 12001.
- 34 H. Geckil, F. Xu, X. Zhang, S. Moon and U. Demirci, *Nanomedicine*, 2010, **5**, 469.
- 35 Z. Hu, Y. Chen, C. Wang, Y. Zheng and Y. Li, *Nature*, 1998, **393**, 149.
- 36 G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.
- 37 A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891.
- 38 K. Rurack, M. Kollmannsberger and J. Daub, *Angew. Chem., Int. Ed.*, 2001, **40**, 385.
- 39 S. Atilgan, I. Kutuk and T. Ozdemir, *Tetrahedron Lett.*, 2010, **51**, 892.
- 40 O. A. Bozdemir, Y. Cakmak, F. Sozmen, T. Ozdemir, A. Siemiarczuk and E. U. Akkaya, *Chem. – Eur. J.*, 2010, **16**, 6346.
- 41 T. Ozdemir, F. Sozmen, S. Mamur, T. Tekinay and E. U. Akkaya, *Chem. Commun.*, 2014, **50**, 5455.
- 42 F. Sozmen, B. S. Oksal, O. A. Bozdemir, O. Buyukcakil and E. U. Akkaya, *Org. Lett.*, 2012, **14**, 5286.
- 43 G. H. Deng, C. M. Tang, F. Y. Li, H. F. Jiang and Y. M. Chen, *Macromolecules*, 2010, **43**, 1191.
- 44 J. Boekhoven, J. M. Poolman, C. Maity, F. Li, L. van der Mee, C. B. Minkenberg, E. Mendes, J. H. van Esch and R. Eelkema, *Nat. Chem.*, 2013, **5**, 433.
- 45 G. Kavanagh and S. Ross-Murphy, *Prog. Polym. Sci.*, 1998, **23**, 533.
- 46 M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature*, **472**, 334.
- 47 T. Z. Forster, *Naturforsch.*, 1949, **4**, 321.
- 48 Z. Kostereli, T. Ozdemir, O. Buyukcakil and E. U. Akkaya, *Org. Lett.*, 2012, **14**, 3636.
- 49 O. A. Bozdemir, S. Erbas-Cakmak, O. O. Ekiz, A. Dana and E. U. Akkaya, *Angew. Chem. Int. Ed.*, 2011, **50**, 10907.



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