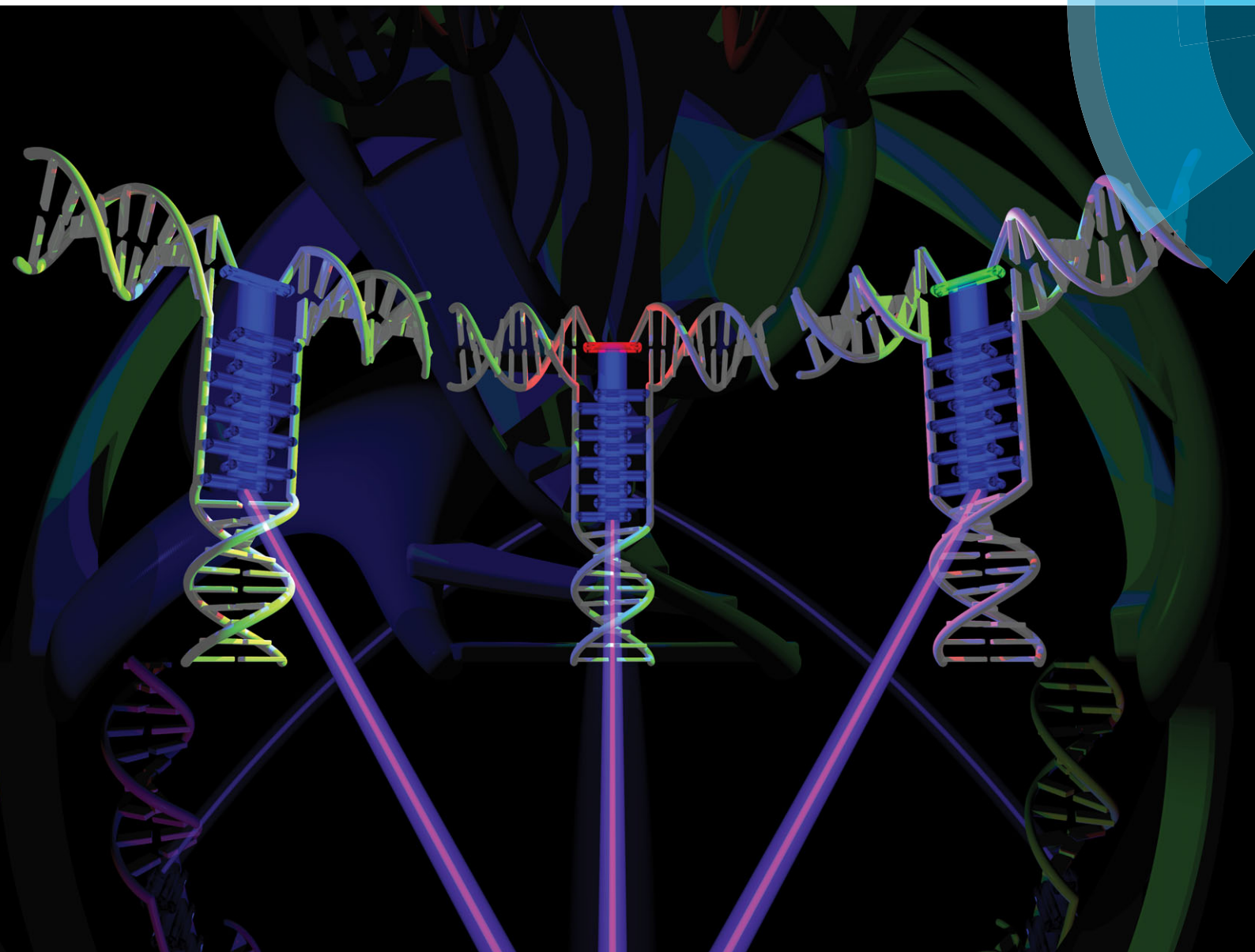


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A modular LHC built on the DNA three-way junction†

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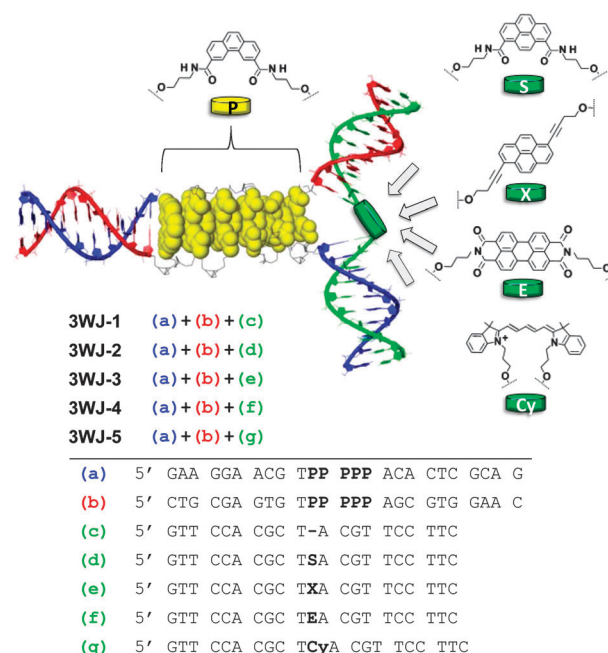
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A light-harvesting complex composed of a π -stacked multichromophoric array in a DNA three-way junction is described. The modular design allows for a ready exchange of non-covalently attached energy acceptors.

In attempts to mimic the naturally occurring process of light harvesting and energy transfer in green plants,^{1–5} scientists are developing artificial systems^{6–17} that allow an efficient transfer of absorbed photons to a collection centre. A key aspect in all efforts is the proper arrangement of suitable chromophores. The field of DNA nano-architectures has received wide attention over the past years. The DNA double helix serves as a scaffold for the controlled arrangement of functional molecules,^{18–23} including a wide range of different chromophores.^{24–32} Also the DNA three-way junction³³ has been exploited for this purpose.^{34–42} Recently, several DNA-based light-harvesting antenna systems have been reported.^{43–51} Here, we describe the use of the DNA three-way junction (3WJ) as a versatile scaffold for the modular construction of an artificial light harvesting complex (LHC).

The architecture of the 3WJ, its sequences and the corresponding building blocks are shown in Scheme 1. The phenanthrene (**P**),⁵² pyrene (**S** and **X**)^{53,54} perylenediimide (**E**),⁵⁵ and the commercially available cyanine (**Cy**) phosphoramidite building blocks were incorporated into the oligomers by automated oligonucleotide synthesis. All oligomers were purified by reverse phase HPLC and analysed by LC-MS (see ESI†). In **3WJ-2**, **-3**, **-4** and **-5**, the LHC is composed of a phenanthrene (**P**) stack, the light absorbing antenna (strands **a** and **b**), and an exchangeable acceptor chromophore (strands **d–g**). **3WJ-1** serves as a control bearing no acceptor dye in the third strand (**c**). Formation of the 3WJs was demonstrated by polyacrylamide gel electrophoresis (ESI†). Thermal denaturation experiments showed a single transition for all 3WJs. Melting temperature (T_m) values ranging from 57–63 °C are listed in Table 1. UV/Vis spectra of the different 3WJs (Fig. 1) reveal the following long-wavelength absorptions of the



Scheme 1 Schematic illustration of the light harvesting 3WJ, the chromophores used and the corresponding sequences.

Table 1 T_m values and fluorescence quantum yields (ϕ_F)^a of 3WJs^b

	3WJ-1	3WJ-2	3WJ-3	3WJ-4	3WJ-5
Acceptor	—	S	X	E	Cy
T_m (°C)	57	59	58	63	59
ϕ_F^c	0.10	0.21	0.32	0.02	0.06 ^d

^a Standard: 2-aminopyridine; for details see ESI. ^b Conditions as in Fig. 1. ^c Phenanthrene excitation (320 nm). ^d Total ϕ_F (1.5% from phenanthrene and 4.9% from Cy emission).

various chromophores: **P** (λ_{max} = 316 nm); **S** (λ_{max} = 353 nm); **X** (λ_{max} = 391 nm); **E** (λ_{max} = 561 nm); and **Cy** (λ_{max} = 652 nm).

The effectiveness of the 3WJs as LHCs was investigated by fluorescence spectroscopy. Fig. 2 shows the emission spectra of **3WJ-1** to **3WJ-4** after excitation of phenanthrene at 320 nm. **3WJ-2** and **3WJ-3**, both of which contain a pyrene derivative as acceptor, exhibit strong

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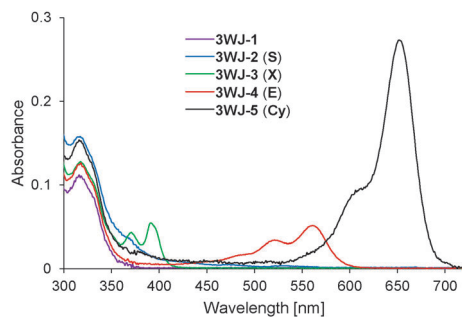


Fig. 1 UV/Vis spectra of the investigated three-way junctions. Conditions: 1 μ M single strand, 100 mM NaCl, 10 mM sodium phosphate buffer, pH 7.0; acceptors are given in brackets.

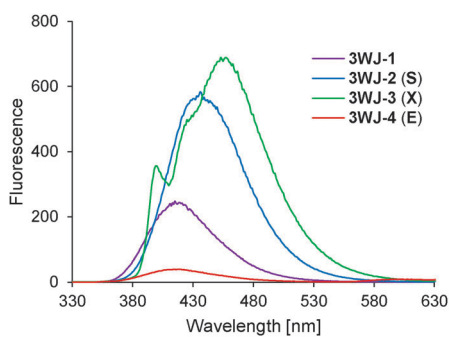


Fig. 2 Fluorescence emission spectra of **3WJ-1**, **3WJ-2**, **3WJ-3** and **3WJ-4**. Conditions: see Fig. 1; λ_{ex} : 320 nm; ex./em. slit: 5 nm.

exciplex emission ($\lambda_{\text{max}} = 435$ and 455 nm, respectively⁵⁶). This is in agreement with the observation made previously with a duplex containing a phenanthrene antenna with a covalently attached pyrene (S).⁴⁶ In the present case, however, the acceptor dye is brought into proximity of the phenanthrene antenna in a non-covalent fashion.

A quantum yield of 0.21 (Table 1) is obtained for **3WJ-2**. Similar results are obtained for **3WJ-3**. However, some pyrene monomer fluorescence (peak at 400 nm and shoulder at around 425 nm) is present in addition to the exciplex emission. The total quantum yield of **3WJ-3** with 1,6-dialkynylpyrene as the acceptor dye is 0.32.

Irradiation of the control **3WJ-1**, which contains the phenanthrene stack but no acceptor chromophore, at 320 nm results in a broad, unstructured emission band centred around 415 nm, which is assigned to phenanthrene excimer fluorescence.^{57–60} Φ_{F} for **3WJ-1** was 0.10 (Table 1). This is considerably less than the values found for **3WJ-2** and **-3** (0.21 and 0.32) that contain a terminal pyrene chromophore.

In three-way junction **3WJ-4**, a perylenediimide unit is used in strand **c**. This chromophore quenches the phenanthrene excimer fluorescence to a considerable extent (Φ_{F} 0.02). The quenching effect^{61,62} is strong, but not as pronounced as in the case of pyrene excimer quenching by the same perylenediimide derivative.^{37,63} The reduced effect can be rationalized by a smaller spectral overlap in the present case (phenanthrene–perylenediimide) than between pyrene and perylenediimide.⁶³

The emission spectra obtained by direct excitation of the two-pyrene acceptor dyes (S or X) are shown in Fig. 3. Excitation was carried out at 370 nm, at which wavelength both pyrene derivatives absorb and phenanthrene excitation is negligible. Two aspects are

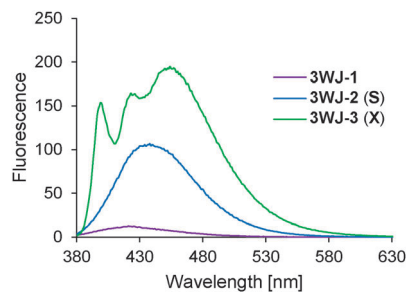


Fig. 3 Fluorescence spectra of **3WJ-1**, **3WJ-2** and **3WJ-3**. Conditions: see Fig. 1. Instrumental set-up as in Fig. 2 (except for λ_{ex} : 370 nm).

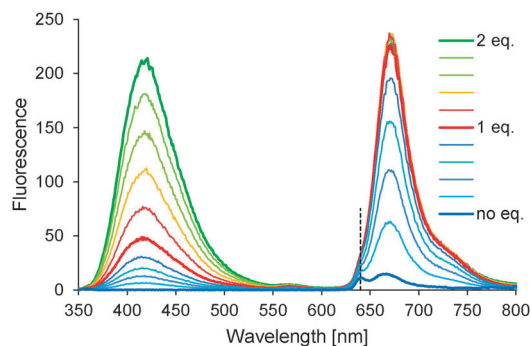


Fig. 4 Build-up of **3WJ-5**: fluorescence spectra after stepwise addition of strands **a** and **b** (1:1-mixture) to single strand **g**. The two strands were pre-annealed and added in 0.2 molar equivalents; an equilibration time of 5 minutes was given before recording the spectrum; other conditions were as shown in Fig. 2. Dashed marker indicates artefacts caused by the second order transmission of the monochromator.

worth noting: (i) the fluorescence intensities are significantly lower than that obtained after excitation of phenanthrene, which shows that the phenanthrene–pyrene 3WJ functions as a LHC; and (ii) the fraction of monomer emission in **3WJ-3** is somewhat larger than after phenanthrene excitation (*cf.* Fig. 2). Furthermore, direct excitation of control **3WJ-1** at 370 nm (Fig. 3) results in no significant fluorescence.

Energy transfer is also observed from phenanthrenes to Cy. Fig. 4 shows the effect of a stepwise build-up of **3WJ-5**. In this experiment, the phenanthrene antenna (*i.e.* a 1:1-mixture of strands **a** and **b**) is added stepwise to the acceptor dye (strand **g**). A gradual increase in Cy fluorescence is observed until antenna and acceptor are present in equimolar concentrations. Phenanthrene excimer emission is also present and grows parallel to Cy fluorescence. Further addition of the antenna beyond the 1:1-ratio does not result in additional growth of Cy fluorescence, while phenanthrene fluorescence grows proportionally. The quantum yields for **P** and **Cy** emission amount to 0.015 and 0.049, respectively (Table 1). **Cy** has no significant absorbance (see ESI,† Fig. S28) at the irradiation wavelength (320 nm) or in the region of phenanthrene emission (360–530 nm). As shown by the corresponding excitation spectra (Fig. 5), phenanthrene excitation (320 nm) leads to **Cy** emission only in **3WJ-5** but not in single strand **g**. These experiments demonstrate that **Cy** fluorescence in **3WJ-5** is due to energy transfer from the phenanthrenes.⁶⁴ A Förster radius of ~ 26 Å is calculated (ESI†). Considering the dimensions of the cavity in a typical 3WJ (~ 12 Å)⁶⁵ as well as its inherent flexibility,^{33,65} energy transfer *via* FRET is, thus, possible. On the other hand, molecular contact between the donor and the acceptor is also



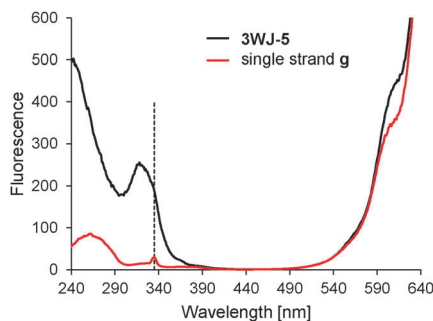


Fig. 5 Fluorescence excitation spectra of **3WJ-5** and single strand **g**. Conditions: Fig. 1; instrumental set-up: Fig. 2, except for λ_{em} : 670 nm; dashed marker: see Fig. 4.

feasible (as e.g. shown by exciplex formation in **3WJ-2** and **-3**) rendering excitation transfer *via* Dexter electron exchange a plausible mechanism.^{61,66}

In conclusion, we have described the construction of LHCs on the basis of the DNA 3WJ. The LHC is based on a modular construction in which a phenanthrene antenna is located in one of the three stems and the acceptor is brought into proximity of the antenna through the annealing of the third strand. Phenanthrene excitation (320 nm) is followed by energy transfer to pyrene, perylene diimide or a cyanine dye. In the case of pyrene, exciplex fluorescence is observed, whereas perylene diimide acts as a quencher. In the case of cyanine, energy transfer leads to cyanine fluorescence. The study demonstrates the use of the DNA 3WJ for the modular assembly of artificial LHCs.

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Notes and references

- D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198–205.
- Light-Harvesting Antennas in Photosynthesis*, ed. B. R. Green and W. W. Parson, Kluwer Acad. Publ., Dordrecht, 2003.
- Artificial Photosynthesis – From Basic Biology to Industrial Applications*, ed. A. F. Collings and C. Critchley, Wiley-VCH, Weinheim, 1st edn, 2005.
- A. Hagfeldt and M. Graetzel, *Acc. Chem. Res.*, 2000, **33**, 269–277.
- I. McConnell, G. H. Li and G. W. Brudvig, *Chem. Biol.*, 2010, **17**, 434–447.
- S. E. Webber, *Chem. Rev.*, 1990, **90**, 1469–1482.
- M. Graetzel, *J. Photochem. Photobiol., C*, 2003, **4**, 145–153.
- V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, **1**, 26–58.
- A. C. Benniston and A. Harriman, *Mater. Today*, 2008, **11**, 26–34.
- B. C. Thompson and J. M. J. Frechet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58–77.
- M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910–1921.
- C. Li, M. Y. Liu, N. G. Pschirer, M. Baumgarten and K. Müllen, *Chem. Rev.*, 2010, **110**, 6817–6855.
- G. Calzaferri, R. Meallet-Renault, D. Brühwiler, R. Pansu, I. Dolamic, T. Diemel, P. Adler, H. R. Li and A. Kunzmann, *ChemPhysChem*, 2011, **12**, 580–594.
- R. W. Wagner and J. S. Lindsey, *J. Am. Chem. Soc.*, 1994, **116**, 9759–9760.
- S. Delahaye, C. Loosli, S. X. Liu, S. Decurtins, G. Labat, A. Neels, A. Loosli, T. R. Ward and A. Hauser, *Adv. Funct. Mater.*, 2006, **16**, 286–295.
- N. Sakai, M. Lista, O. Kel, S. Sakurai, D. Emery, J. Mareda, E. Vauthay and S. Matile, *J. Am. Chem. Soc.*, 2011, **133**, 15224–15227.
- V. Garg, G. Kodis, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore and D. Gust, *J. Phys. Chem. B*, 2013, **117**, 11299–11308.
- N. C. Seeman, *Annu. Rev. Biochem.*, 2010, **79**, 65–87.
- C. K. McLaughlin, G. D. Hamblin and H. F. Sleiman, *Chem. Soc. Rev.*, 2011, **40**, 5647–5656.
- M. Endo and H. Sugiyama, *ChemBioChem*, 2009, **10**, 2420–2443.
- M. A. Campbell and J. Wengel, *Chem. Soc. Rev.*, 2011, **40**, 5680–5689.
- B. Sacca and C. M. Niemeyer, *Angew. Chem., Int. Ed.*, 2012, **51**, 58–66.
- M. Famulok and G. Mayer, *Acc. Chem. Res.*, 2011, **44**, 1349–1358.

- V. V. Filichev and E. B. Pedersen, in *Wiley Encycl. Chem. Biol.*, 1, ed. T. P. Begley, Wiley, Hoboken, 2009, pp. 493–524.
- R. Varghese and H. A. Wagenknecht, *Chem. Commun.*, 2009, 2615–2624.
- V. L. Malinovskii, D. Wenger and R. Häner, *Chem. Soc. Rev.*, 2010, **39**, 410–422.
- T. J. Bandy, A. Brewer, J. R. Burns, G. Marth, T. Nguyen and E. Stulz, *Chem. Soc. Rev.*, 2010, **40**, 138–148.
- E. Schwartz, S. Le Gac, J. J. L. M. Cornelissen, R. J. M. Nolte and A. E. Rowan, *Chem. Soc. Rev.*, 2010, **39**, 1576–1599.
- H. Kashida and H. Asanuma, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7196–7204.
- Y. N. Teo and E. T. Kool, *Chem. Rev.*, 2012, **112**, 4221–4245.
- M. E. Ostergaard and P. J. Hrdlicka, *Chem. Soc. Rev.*, 2011, **40**, 5771–5788.
- C. Dohno and K. Nakatani, *Chem. Soc. Rev.*, 2011, **40**, 5718–5729.
- D. M. J. Lilley, *Q. Rev. Biophys.*, 2000, **33**, 109–159.
- M. H. Hansen, P. Blakskjaer, L. K. Petersen, T. H. Hansen, J. W. Hojfeldt, K. V. Gothelf and N. J. V. Hansen, *J. Am. Chem. Soc.*, 2009, **131**, 1322–1327.
- I. T. Seemann, V. Singh, M. Azarkh, M. Drescher and J. S. Hartig, *J. Am. Chem. Soc.*, 2011, **133**, 4706–4709.
- H. Xiong, P. Leonard and F. Seela, *Bioconjugate Chem.*, 2012, **23**, 856–870.
- M. Probst, D. Wenger, S. M. Biner and R. Häner, *Org. Biomol. Chem.*, 2012, **10**, 755–759.
- J. L. Duprey, Y. Takezawa and M. Shionoya, *Angew. Chem., Int. Ed.*, 2013, **52**, 1212–1216.
- W. Su, C. R. Bagshaw and G. A. Burley, *Sci. Rep.*, 2013, **3**, 1883, DOI: 10.1038/srep01883.
- P. Kumar, K. I. Shaikh, A. S. Jorgensen, S. Kumar and P. Nielsen, *J. Org. Chem.*, 2012, **77**, 9562–9573.
- O. Reinstein, M. A. Neves, M. Saad, S. N. Boodram, S. Lombardo, S. A. Beckham, J. Brouwer, G. F. Audette, P. Groves, M. C. Wilce and P. E. Johnson, *Biochemistry*, 2011, **50**, 9368–9376.
- L. Feng, C. Zhao, Y. Xiao, L. Wu, J. Ren and X. Qu, *Chem. Commun.*, 2012, **48**, 6900–6902.
- O. N. Sancho, W. R. Browne and G. Roelfes, *Chem.–Eur. J.*, 2013, **19**, 2457–2461.
- P. K. Dutta, R. Varghese, J. Nangreave, S. Lin, H. Yan and Y. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 11985–11993.
- B. Albinsson, J. K. Hannestad and K. Boerjesson, *Coord. Chem. Rev.*, 2012, **256**, 2399–2413.
- F. Garo and R. Häner, *Angew. Chem., Int. Ed.*, 2012, **51**, 916–919.
- O. O. Adeyemi, V. L. Malinovskii, S. M. Biner, G. Calzaferri and R. Häner, *Chem. Commun.*, 2012, **48**, 9589–9591.
- J. G. Woller, J. K. Hannestad and B. Albinsson, *J. Am. Chem. Soc.*, 2013, **135**, 2759–2768.
- C. M. Spillmann, M. G. Ancona, S. Buckhout-White, W. R. Algar, M. H. Stewart, K. Susumu, A. L. Huston, E. R. Goldman and I. L. Medintz, *ACS Nano*, 2013, **7**, 7101–7118.
- Charge Transfer in DNA – From Mechanism to Application*, ed. H. A. Wagenknecht, Wiley-VCH, Weinheim, Germany, 2005.
- P. V. Kumar and M. Duff, *J. Am. Chem. Soc.*, 2009, **131**, 16024–16026.
- S. M. Langenegger and R. Häner, *ChemBioChem*, 2005, **6**, 848–851.
- S. M. Langenegger and R. Häner, *Chem. Commun.*, 2004, 2792–2793.
- H. Bittermann, D. Siegemund, V. L. Malinovskii and R. Häner, *J. Am. Chem. Soc.*, 2008, **130**, 15285–15287.
- N. Rahe, C. Rinn and T. Carell, *Chem. Commun.*, 2003, 2119–2121.
- The slight differences are attributed to changes in the linkers, *i.e.* carboxamide *vs.* alkynyl-substituents.
- Y. Nakamura, T. Yamazaki and J. Nishimura, *Org. Lett.*, 2005, **7**, 3259–3262.
- F. D. Lewis and E. L. Burch, *J. Photochem. Photobiol., A*, 1996, **96**, 19–23.
- J. B. Birks, in *The Exciplex*, ed. M. Gordon and W. R. Ware, Academic Press Inc., New York, 1975, pp. 39–73.
- F. M. Winnik, *Chem. Rev.*, 1993, **93**, 587–614.
- P. Ceroni and V. Balzani, in *The Exploration of Supramolecular Systems and Nanostructures by Photochemical Techniques*, 78, ed. P. Ceroni, Springer, 2012, pp. 21–38.
- J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, Singapore, 3rd edn 2006.
- N. Bouquin, V. L. Malinovskii and R. Häner, *Chem. Commun.*, 2008, 1974–1976.
- D. Pevenage, M. Van der Auweraer and F. C. De Schryver, *Chem. Phys. Lett.*, 2000, **319**, 512–520.
- T. Sabir, A. Toulmin, L. Ma, A. C. Jones, P. McGlynn, G. F. Schröder and S. W. Magennis, *J. Am. Chem. Soc.*, 2012, **134**, 6280–6285.
- D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836–850.

