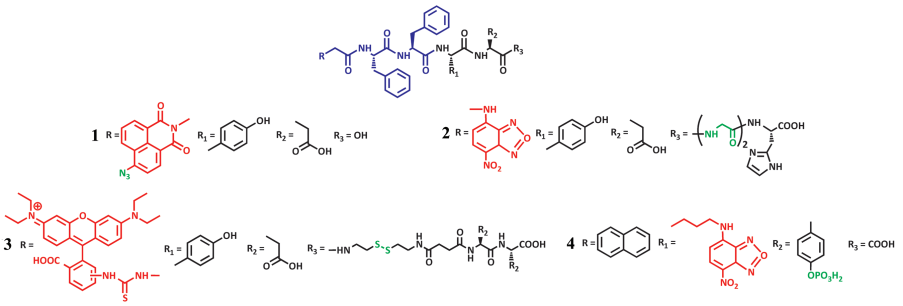

Fig. 1. Chemical structure of probes used in self-assembly dependent imaging. The unit that drives the self-assembly is presented in blue, the fluorophore in red and the biologically sensitive groups are marked in green: they can be incorporated in the fluorescent group (Cai et al. 2016), in the peptide portion of the amphiphile (Cai et al. 2014; Wang et al. 2015) or attached as a separate unit (Gao et al. 2012; Gao et al. 2013a; Gao et al. 2013b).

J-aggregate assemblies an end-to-end arrangement is observed, i.e., the transition moments of the monomers are aligned parallel to the line joining their centres, and this organisation results in a narrow bathochromic shift (red shift), known as J-band (Zhai et al. 2014). Besides these shifts, the self-assembly is generally associated with the quenching of the fluorescence signal (weakens the read out signal). Although this may seem to be a drawback, the aggregation induced quenching is often used in the development of probes (Kiyonaka et al. 2004; Zhai et al. 2014). The opposite process—disassembly—has received much less attention as a sensing mechanism (Mizusawa et al. 2010; Zhai et al. 2014). This process, however, is quite relevant in the case of approaches using supramolecular structures, for which the disassembly results in enhancing the read-out signal and can be used for the design of turn-on probes (Mizusawa et al. 2010). In addition to these changes in the fluorescent properties, the self-assembly process influences dramatically the contrast in fluorescent imaging (Gao et al. 2012). Upon excitation, the dissolved unassembled probe emits identically in each direction within the optical thickness of the focal plan resulting in little contrast for imaging. The directional self-assembly of the probes leads to localization of the fluorophores within the assembled nanofibers and thus, provide excellent contrast for imaging of these assemblies. These changes in the fluorescence read-out signal upon self-assembly have inspired the development of several approaches for cancer diagnosis and imaging *in vitro* and *in vivo*.

Biocatalytic self-assembly (BSA) for diagnosis and imaging

BSA merges the efficiency and selectivity of an enzymatic transformation with the sensitivity of the self-assembly process. The concept was first introduced in 2004 by Xu's group (Yang et al. 2004; Yang and Xu 2004). In these first studies, the sol-gel transition state that is easily visible by naked eye was applied as a simple detection method for the presence of an enzyme—phosphatase and its inhibitors. This pioneering work was vastly explored in the following years (Thornton et al. 2009; Thornton et al. 2013) and used in different analytical methodologies involving phosphatases (Gao et al. 2013a; Du et al. 2015a; Gao et al. 2013b; Gao et al. 2012; Zhou and Xu 2015; Yang