

DONOR-SUBSTITUTED PYRIDOBENZO(BIS)THIAZOLES AS TWO-PHOTON ABSORBING FLUOROPHORES FOR BIOIMAGING

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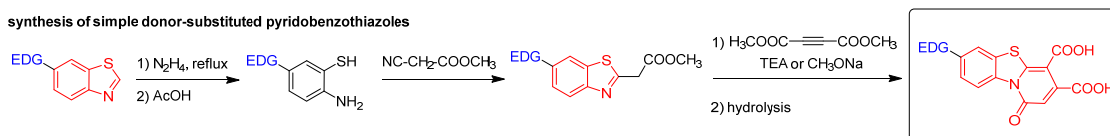
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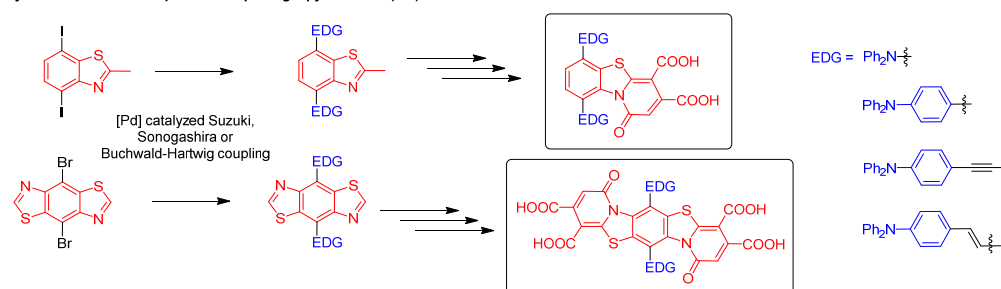
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π -Conjugated compounds based on benzothiazoles substituted with electron-donating (EDG) or electron-withdrawing (EWG) groups are used as dyes in various fields of optoelectronics [1,2]. A series of novel donor-substituted benzothiazoles and benzobisthiazoles has been prepared from 6-bromobenzothiazole, 4,7-diiodo-2-methylbenzothiazole and 4,8-dibromobenzo[1,2-*d*:4,5-*d'*]bisthiazole via palladium-catalyzed Sonogashira and Suzuki cross-coupling reactions. The thiazole ring in these compounds was cleaved to obtain corresponding aminothiophenols, which were reacted with methyl cyanoacetate to afford donor-substituted benzo(bis)thiazoles with activated methylene groups. Target fluorophores with one or two 2-pyridone ring(s) annulated to the central benzo(bis)thiazole moiety were prepared by Michael addition of these methylene activated compounds to dimethyl acetylene-dicarboxylate, followed by hydrolysis of the prepared esters to carboxylic acids. These dyes exhibit extremely high fluorescence quantum yields also in water (in particular in the form of carboxylate salts) and are computed to display large two-photon absorption (TPA) cross-sections ($> 1000 \text{ GM}$) in the near-IR region. These properties make them attractive as water-soluble diagnostic agents in a high-resolution laser fluorescence microscopy.

synthesis of simple donor-substituted pyridobenzothiazoles



synthesis of TPA fluorophores comprising a pyridobenzo(bis)thiazole core



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[1] Hrobárik, P.; Hrobáriková, V.; Sigmundová, I. et al. *J. Org. Chem.* **2011**, 76, 8726–8736.

[2] Hrobáriková, V.; Hrobárik, P.; Gajdoš, P. et al. *J. Org. Chem.* **2010**, 75, 3053–3068.