6,8-Diarylimidazo[1,2-a]pyrazin-3(7H)-ones as potential chemiluminescent pH/superoxide double sensors

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Imidazo[1,2-a]pyrazin-3(7H)-ones possessing different para-substituted phenyl groups at 6- and 8-positions were synthesized, and their superoxide-triggered chemiluminescence was investigated using the hypoxanthine-xanthine oxidase system as the source of superoxide in the phosphate buffer under various pH conditions. 2-Methyl-6-(4-methoxyphenyl)-8-(4-trifluoromethylphenyl)imidazo[1,2-a]pyrazin-3(7H)-one (1a) showed chemiluminescence around 460 nm under neutral conditions. This luminescence was ascribed from the singlet-excited state of 2-acetamido-5-(4-methoxyphenyl)-3-(4-trifluoromethylphenyl)pyrazine (2a), the product of the chemiluminescent reaction of 1a with superoxide. On raising the pH of the buffer solution, the emission at 540 nm was increased with decreasing the emission at 460 nm. This largely bathochromic-shifted luminescence was produced from the singlet-excited amide anion of 2a, in which large energy stabilization with extended conjugation at the 8-position is supposed to cause the large shift in the emission maximum. Also the electron-withdrawing trifluoromethyl group, which can stabilize the anion, would be responsible for the red-shifted luminescence. The other imidazopyrazinones, 6-(4-hydroxyphenyl)-(1b) and 6-(4-dimethylaminophenyl)-derivatives (1c), showed no luminescence under the same conditions, probably because the specific interaction between the solvating water and the hydroxyl or dimethylamino group quenches their emission. The observed pH-dependent bimodal chemiluminescence of 1a may allow us to apply 1a for spontaneous detection of superoxide and the local pH in a cell or in a droplet.