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Highly stable and fluorescent switching spirooxazines

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Abstract—Two novel photochromic spirooxazines, **SO-NA1** and **SO-NA2**, containing a naphthalimide unit were synthesized. The imide group of naphthalimide unit is incorporated at the naphthoxazine fragment, thus giving strong electron-withdrawing effect favoring the long-lived merocyanine (MC) in the dark giving good colorability in solution. Remarkably, their open merocyanine (MC) forms exhibit significantly long lifetimes, almost three magnitudes longer than that of unsubstituted spironaphthoxazine (**1**). Moreover, the fluorescence of naphthalimide unit can be switched *on* and *off* by photoinduced conversion between the open and closed forms.

1. Introduction

Photochromic organic compounds have been widely studied over the past decades because of their potential application in various photoactive devices such as optical memory, optical switchers, displays and non-linear optics.[1–3] Spirooxazines (SO)[4,5] are well-known photochromic compounds of interest from the viewpoint of fundamental elucidation of photochemical reactions and potential applications in optical memories. However, in the past decades, the application of spirooxazine in optical memory has been hindered by the short lifetime of the colored photomerocyanine species, which reverts thermally to the ring-closed colorless spirooxazine with an apparent activation energy of 14–30 kcal/mol.[5] Therefore, various methods to stabilize the photomerocyanine form have been developed.[6] Molecular orbital calculations and NMR-NOE experiments have been carried out to establish the most stable colored structure of spironaphthoxazine as the quinoidal form TTC (Scheme 1).[1a,c] The poor thermal stability of the open form may result from the exorbitant electron density of the oxygen atom in the naphthalene ring. Hence a simple method to improve the thermal stability of the open-ring merocyanine (MC) form could be realized by decreasing the electron density of the oxygen atom via introducing electron-withdrawing groups or hetero atoms to the naphthalene ring.

We herein report on the use of a fluorescent intermediate of 3-amino-4-hydroxy-1,8-naphthalimide as the spironaphthoxazines framework (**SO-NA1** and **SO-NA2** in Scheme 1). The naphthalimide unit is incorporated at the naphthoxazine fragment, thus giving a strong electron-withdrawing effect favoring the long-lived MC in the dark and giving good colorability in solution. As expected, significant stabilization of the photomerocyanine was observed. Remarkably, their open MC forms are stable with long lifetimes. Moreover, the fluorescence of naphthalimide unit can be switched *on* and *off* by photoinduced conversion.

2. Results and discussion

The synthesis of spironaphthoxazines (**SO-NA1** and **SO-NA2**) is straightforward, starting from 4-bromo-1,8-naphthalic anhydride as shown in Scheme 2. The key intermediate of 3-amino-4-hydroxy-1,8-naphthalimide was synthesized via four steps by the established literature procedure.[7] The chemical structures of **SO-NA1** and **SO-NA2** are characterized fully by ^{1}H NMR, ^{13}C NMR, and HRMS.

Ultraviolet irradiation of **SO-NA1** and **SO-NA2** at the wavelength of 365 nm results in the photochromism. The increase of absorption intensity in the visible range corresponds to the open MC (Scheme 1), which can be evidenced from ^{1}H NMR spectral analysis before and after irradiation at room temperature.[8,9] In the case of **SO-NA1**, the distinct character of spirooxazine is the *gem*-dimethyl group in the indole fragment, which is shifted toward low field from 1.35 and 1.37 ppm (the closed form SO) to 1.87 ppm (the open form MC). This corresponds to the trans-stereoisomer of the colored planar forms in which the lone electron-pair of the azomethinic nitrogen then affects the electronic environment strongly.[8] Upon continuous UV irradiation of **SO-NA1** and **SO-NA2**, the resulting long-wavelength bands in the stationary absorption spectra have unsymmetrical shape.

Keywords: Spirooxazines; Photochromism; Synthesis; Fluorescence; Switching.
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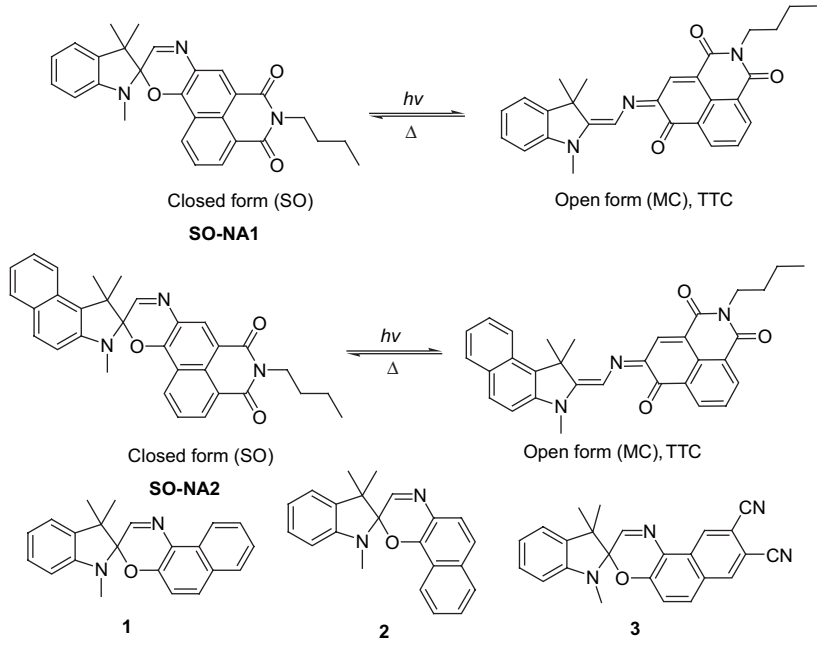
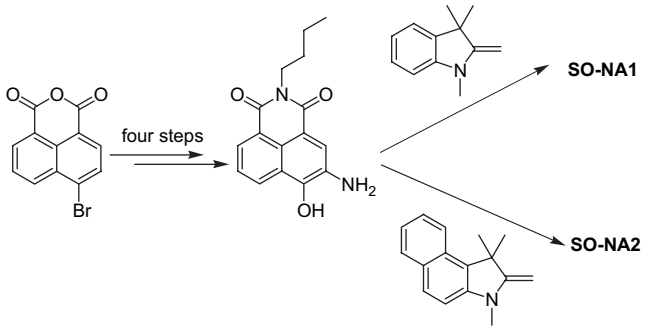


Scheme 1. Photochromic transformation of **SO-NA1** and **SO-NA2**, and reference compounds **1**, **2** and **3**.



Scheme 2. Synthetic route of **SO-NA1** and **SO-NA2**.

For instance, the electronic absorption spectrum of **SO-NA2** in the range of 400–700 nm in cyclohexane is characterized by unusually broad long-wavelength absorption with two peaks at 620 and 668 nm. The peak on the short-wavelength side becomes less distinct in toluene and then finally diminished in high polar solvent like isopropanol (Fig. 1). Such solvatochromic behavior is induced by variation in the polarity of the medium, showing itself as pronounced changes in the position and intensity of their UV–vis absorption bands. The colorless solution of **SO-NA2** in cyclohexane corresponds only to the closed form. Furthermore, **SO-NA1** and **SO-NA2** exhibit the solvatochromism to the same extent in polar solvents, such as isopropanol (Fig. 1b). Obviously, **SO-NA1** and **SO-NA2** show negative solvatochromism, that is, the long-wavelength peak in the visible range is shifted hypsochromically when increasing the solvent polarity (Table 1). The electron-withdrawing imide group of the naphthalimide unit in the naphthoxazine moiety would be expected to favorably delocalize the negative charge on the oxygen atom.[1,5a] From the analysis of the dependence of the spectral characteristics of **SO-NA1** and **SO-NA2** the polar properties can be estimated using the empirical Brooker parameters (χ_R and χ_B) of the solvents. Interestingly, there is a correlation between the wave

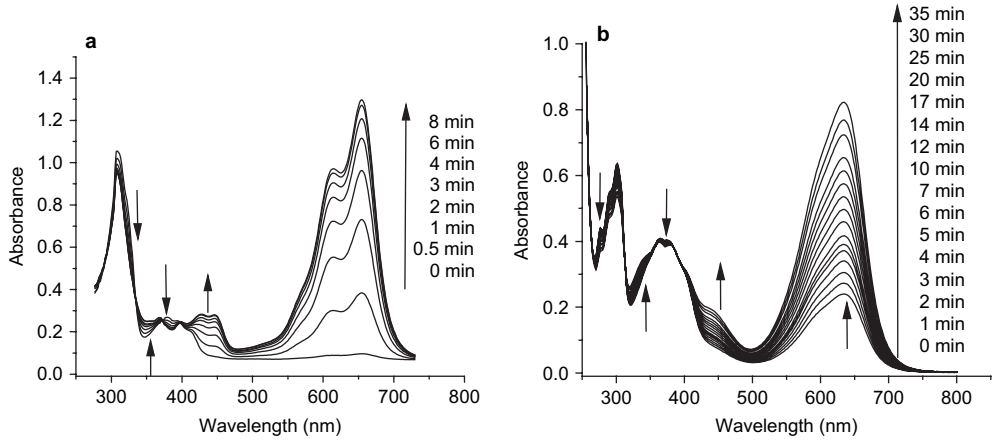


Figure 1. Absorption spectra of photochromic compound **SO-NA2** at 25 °C: (a) during UV light irradiation at 365 nm in toluene (2.5×10^{-5} mol L^{-1}) and (b) during UV light irradiation at 365 nm in isopropanol (5.0×10^{-5} mol L^{-1}).

Table 1. Wavelengths of maximum absorption (λ_{max}) of the colored merocyanine forms of **SO-NA1** and **SO-NA2** and reference compound **3** in different solvents for the visible area

Compounds	λ_{max}/nm				
	Toluene	Cyclohexane	Methylene chloride	Isopropanol	Acetonitrile
SO-NA1	610, 653	605, 650	590 (sh), 639	620	550 (sh), 621
SO-NA2	622, 667	620, 668	607 (sh), 652	635[b]	585 (sh), 635
3[a]	620	612	—	—	612

[a] The data were taken from Ref. 1c.
[b] The molar extinction coefficient ε value of ca. 6.2×10^4 mol^{-1} L cm^{-1} was used ($A=\varepsilon lrC_j$, r is the ratio of the MC form, C_j is the concentration of original SO form). A and r are determined from the data when the solution was irradiated for 15 min.

numbers of the absorption maxima of the acyclic isomers and the parameters χ_B (Fig. 2), whereas a correlation with the parameters χ_R is lacking, indicative of the negative solvatochromism.[1c,10]

For most spironaphthoxazines, the equilibrium between cyclic SO and ring-opening MC is substantially shifted toward the cyclic form. Since the decay of photoisomerization upon dark thermal relaxation is quite well fitted to the exponential function (Fig. 3), the half-life of **SO-NA1** and **SO-NA2** can be easily obtained by fitting with first order decay (listed in Table 2). The parent, unsubstituted spironaphthoxazines **1** and **2** turn blue upon irradiation both in liquid or solid, and rapidly fade back to colorless when the activating irradiation is removed. Actually, the lifetime of the colored form is only a few seconds for **1** and **2** at room temperature (Table 2).[5a,11] In contrast, both the open forms of the synthesized **SO-NA1** and **SO-NA2** exhibit significantly long lifetime, almost three magnitudes longer in toluene than that of parent compound **1** under the dark thermal relaxation. The half-life of the colored form of **SO-NA2** surprisingly reaches nearly 10^4 s in isopropanol at room temperature (Table 2). Furthermore, the thermal relaxation of **SO-NA1** and **SO-NA2** in the dark is an order of magnitude longer than that of compound **3**[1c] (Table 2), which indicates that the contribution to the increase of MC lifetime by two nitrile groups is much less than that by the imide group of spironaphthoxazines for the two given compounds. For **SO-NA2**, the lifetime increase of the open MC form can be further attributed to the benzene annelation of the indoline moiety. The solvents have an ambiguous effect on the lifetime of the reverse reaction of SO, which is determined by the electron-donating and electron-withdrawing properties of substituents in the heterocyclic and oxazine fragments.[5a] In the case of **SO-NA1** and **SO-NA2** containing electron-withdrawing imide substituent in the naphthoxazine fragment and an electron-donating benzene annelation in the indoline fragment, the life-time increases in parallel with the polarity of the solvent. For **SO-NA2**, the half-life of the colored form was a few minutes in low polarity solvent like cyclohexane and it was

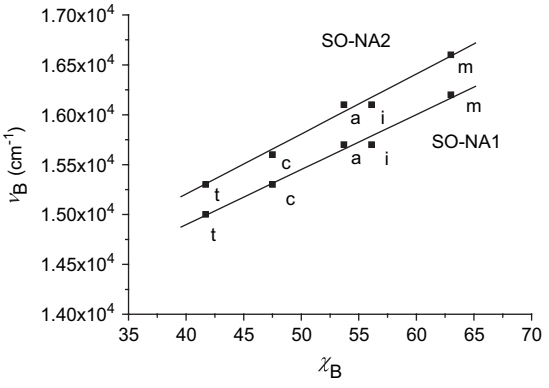


Figure 2. Visualization of significant linear relationships between the wave numbers ν_B of the absorption maximum of the open forms and the Brookers solvatochromic parameters χ_B (blue shift) for methanol (m), isopropanol (i), methylene chloride (c), acetonitrile (a), and toluene (t).

Table 2. Half-life $\tau_{1/2}$ (s) of colored SO in dark decoloration in different solvents at 25 °C

Compounds	Cyclohexane	Toluene	Isopropanol
	$\tau_{1/2}$[c]	$\tau_{1/2}$[c]	$\tau_{1/2}$[c]
SO-NA1	263	2100	—
SO-NA2	407	2355	9748
1[a]	3.8	3.6	—
3[b]	58.7	365	—

[a] The data were taken from Ref. 5a.
[b] The data were taken from Ref. 1c.
[c] $\tau_{1/2}$ was calculated using first order kinetics fitting.

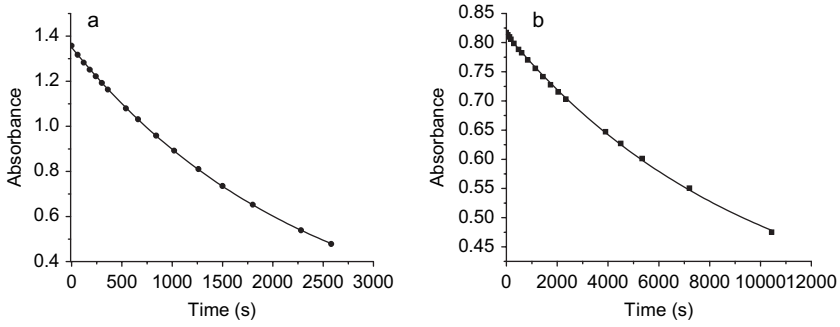


Figure 3. Thermal relaxation kinetics of **SO-NA2** solutions in the dark at 25 °C: (a) in toluene at 667 nm with half-life of 2353±41 s and (b) in isopropanol at 635 nm with half-life of 9748±397 s.

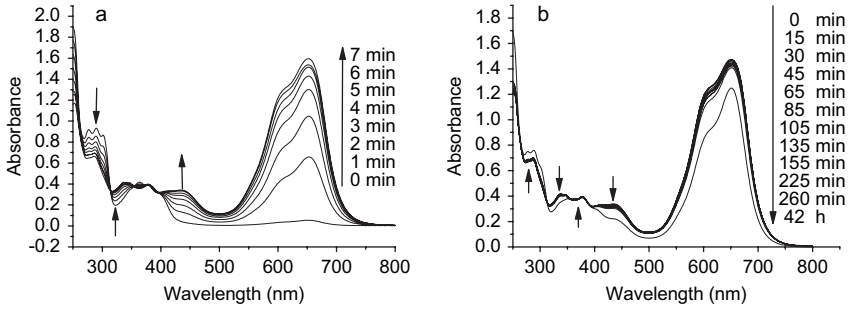


Figure 4. Absorption spectra of PMMA matrix containing **SO-NA2** at 25 °C (1% by weight): (a) during UV light irradiation at 365 nm and (b) in the dark after being irradiated.

prolonged to several hours in high polarity solvent like isopropanol. Similarly, the ultra-slow thermal-bleaching of the open MC forms of **SO-NA1** and **SO-NA2** in the PMMA matrix (1% by weight) was also observed (Fig. 4). In addition, the absorption change of **SO-NA1** and **SO-NA2** remains almost constant upon multiple irradiation cycles, indicative of reversibility and fatigue-resistance (Fig. 5).

The electron-withdrawing imide group at the naphthoxazine moiety further results in a distinctive long-wavelength shift in the colored form with respect to their parent photochromic compound **2**.[5a,11] In **SO-NA2**, the benzene annelation on the indoline fragment also gives a delocalization increase to enhance the shift. In combination, these two effects cause the colored MC form of **SO-NA2** to absorb at unusually long wavelength. The open form of **SO-NA2** in cyclohexane absorbs at 668 nm, which is 90 nm longer than the unsubstituted spirooxazine **1**.

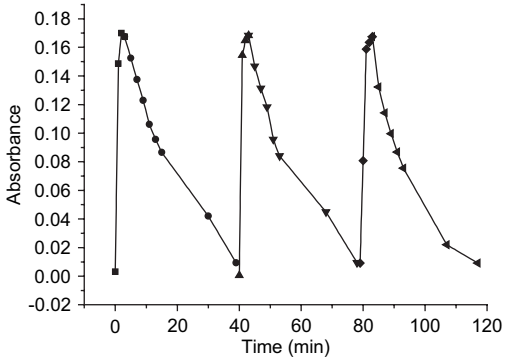


Figure 5. Time-dependent photocoloration of **SO-NA2** in cyclohexane (2×10^{-5} mol L^{-1}) at 25 °C by UV irradiation at 365 nm and the subsequent thermal fading when the irradiation is turned off. The monitored wavelength is 668 nm.

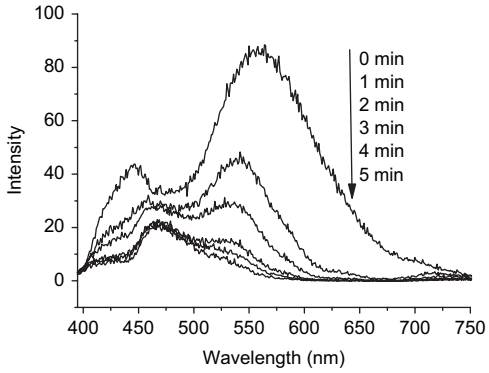


Figure 6. Fluorescence changes of **SO-NA2** in toluene (2×10^{-5} mol L^{-1}) at 365 nm during irradiation.

It is known that 1,8-naphthalimides (NP) are highly fluorescent with high chemical stability.[12,13] Interestingly, the fluorescence of naphthalimide unit in **SO-NA1** and **SO-NA2** can be switched *on* and *off* by photoinduced conversion between the open and closed forms. That is, the closed form of **SO-NA2** shows the characteristic fluorescence from naphthalimide unit at 560 nm, which diminishes quickly under the UV irradiation (Fig. 6). During the dark decoloration, the fluorescence of the solution can be recovered slowly and the process is repeatable. The luminescence quenching of naphthalimide unit in the open form of **SO-NA1** and **SO-NA2** may result from the electronic delocalization throughout the MC molecule.[14]

A common method to determine the molar extinction coefficient of MC form in spirooxazine in visible area is by NMR spectroscopy at low temperature.[8,15] However, the molar extinction coefficient of the open form MC is always difficult to be obtained since it is inconvenient to determine the concentration of the MC form due to the thermal-bleaching reaction.[1a,5] Here we develop a method to determine the proportion of the open form based on the HPLC technique. As mentioned above, the half-life of the colored **SO-NA2** in dark decoloration in isopropanol is 163 min. The HPLC retention time eluted by isopropanol at a flow rate of 1.0 mL/min is 1.9 and 2.2 min for the open and closed form of **SO-NA2** (Fig. 7), respectively. Therefore, the

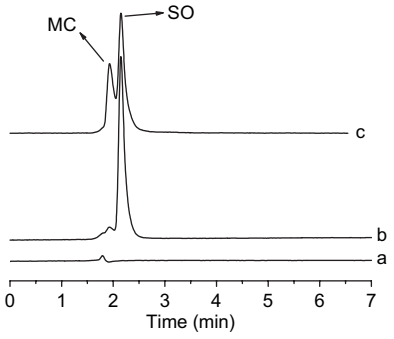


Figure 7. HPLC traces of **SO-NA2** (in isopropanol, 2.0×10^{-5} mol L^{-1}) at 25 °C eluted by isopropanol at a flow rate of 1.0 mL/min detected at the isobestic wavelength of 385 nm: (a) isopropanol as blank, (b) before UV light irradiation, and (c) under UV light irradiation at 365 nm until reaching photostationary state.

decoloration of thermal relaxation to the closed form during HPLC determination could be neglected with respect to the long lifetime of MC form. When we set the isobestic absorption point as the detecting wavelength, the molar ratio between the colored form and the colorless form is equal to the integrated area of HPLC peaks. Therefore, before UV light irradiation (Fig. 7b), the constant of thermal equilibrium (k_T=[MC]$_T$/[SO]$_T$) for **SO-NA2** is 0.054, obtained from the corresponding integrated areas of HPLC peaks. Similarly, the constant of photostationary state equilibrium (k_{UV}=[MC]$_{UV}$/[SO]$_{UV}$) can be obtained as 0.552 under UV light irradiation at 365 nm until it reaches photostationary state (Fig. 7c). Hence the photocolorability[9,15] ($\Delta k_{UV}=k_{UV}-k_T$), defined as the difference between the thermal equilibrium constant (k_T) and the photostationary states (k_{UV}), is 0.498, indicative of high colorability. The molar extinction coefficient of **SO-NA2** (6.2×10^4 mol^{-1} L cm^{-1}) can be further obtained from HPLC analysis. Notably, the ideal time for determining the ratio using the HPLC method in this system (at least 2.2–3 min) is almost the same or comparable to that of ^{1}H NMR measurements, but there are advantages over the method of ^{1}H NMR: (1) the ideal detecting concentration for ^{1}H NMR is generally at least 10^{-3} mol L^{-1} for quick determination in a few minutes, (2) in order to determine the molar extinction coefficient, it is better to determine the open form ratio and absorption in the same order of magnitude of the concentration, which can eliminate the assumption that the ratio is unchanged for the different concentration (10^{-3} mol L^{-1} for ^{1}H NMR and 10^{-5} mol L^{-1} for UV–vis).[8]

3. Conclusions

Fluorescent modulation can be successfully realized by two novel spirooxazines containing a naphthalimide unit in oxazine fragment. Remarkably, the electron-withdrawing imide group of naphthalimide unit incorporated at the naphthoxazine moiety results in the open MC forms exhibiting significantly long lifetimes. The series of spirooxazines containing naphthalimide in oxazine fragments widely extends the available range of photochromic properties. The almost bistable states of these compounds with fluorescent modulation show great prospects in potential application, such as molecular switches and information storage.[14]

4. Experimental

4.1. General

4-Bromo-1,8-naphthalic anhydride, 1,3,3-trimethyl-2-methyleneindoline, and 1,3,3-trimethyl-2-methylene-2,3-dihydro-1*H*-benzo[*e*]indole were commercially available and purified before use. All other reagents were of analytical purity and used without further treatment. Melting points were measured on X4 Micro-melting point apparatus. ^{1}H NMR spectra were recorded on a Brucker AM-500 spectrometer. MS were recorded on an ESI mass spectroscopy. Absorption and fluorescence spectra were recorded on Varian Cary 500 and Varian Cary Eclipse, respectively. HPLC analyses were determined by Agilen 1100 eluted by isopropanol at a flow rate of 1.0 mL/min.

4.1.1. 1,3,3-Trimethyl-spiro[indolino-2,2′-[2*H*]-*N*-butyl-benzo[1′,2′,3′-4,4a,5]isoquinolio[6,7-*b*][1,4]oxazine-6′,8′-dione] (SO-NA1). The mixture of *N*-butyl-4-hydroxy-3-amino-1,8-naphthalimide (0.28 g, 0.985 mmol) and 1,3,3-trimethyl-2-methyleneindoline (0.17 g, 0.982 mmol), $NaHCO_3$ (0.4 g, 4.8 mmol), $MgSO_4$ (0.3 g, 2.5 mmol), DMSO (0.192 g, 2.46 mmol), and toluene (60 mL) were reacted for 6 h at 80 °C under the protection of argon atmosphere. The resulting solution was filtered and the solvent was removed by vacuum rotation evaporator. The product was purified by column chromatography on silica gel eluting with ether/ethyl acetate (4:1 v/v) to give **SO-NA1** (0.025 g, yield 5.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (t, J=7.4 Hz, 3H, –CH_2CH_3), 1.35 (s, 3H, –CH_3), 1.37 (s, 3H, –CH_3), 1.42–1.47 (m, 2H, –CH_2CH_3), 1.69–1.72 (m, 2H, –NCH_2CH_2–), 2.80 (s, 3H, –NCH_3), 4.17 (t, J=7.6 Hz, 2H, –NCH_2CH_2–), 6.63 (d, J=7.7 Hz, 1H, Ph-H), 6.96 (t, J=7.4 Hz, 1H, Ph-H), 7.13 (d, J=7.3 Hz, 1H, Ph-H), 7.26 (t, 1H, J=6.6 Hz, Ph-H), 7.60 (t, J=7.4 Hz, 1H, naphthalimide-H), 7.83 (s, 1H, naphthalimide-H), 8.28 (d, J=8.4 Hz, 1H, naphthalimide-H), 8.55 (d, J=7.3 Hz, 1H, naphthalimide-H), 8.67 (s, 1H, N=CH); ^{13}C NMR (500 MHz, $CDCl_3$): 14.52, 21.07, 21.36, 26.32, 30.28, 30.93, 40.89, 53.04, 101.34, 108.10, 116.27, 121.10, 122.26, 122.62, 123.53, 126.81, 127.11, 128.77, 128.92, 130.03, 132.62, 132.84, 136.00, 147.77, 148.57, 154.21, 164.22, 164.87; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{28}N_3O_3$: 454.2131 [M$^+$+H], found: 454.2129.

4.1.2. 1,3,3-Trimethyl-spiro[benzo[1,2-*e*]indolino-2,2′-[2*H*]-*N*-butyl-benzo[1′,2′,3′-4,4a,5]isoquinolino[6,7-*b*][1,4]oxazine-6′,8′-dione] (SO-NA2). SO-NA2 was prepared by similar procedure of **SO-NA1** with the yield of 9.8%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (t, J=7.3 Hz, 3H, –CH_2CH_3), 1.41–1.49 (m, 2H, –CH_2CH_3), 1.60 (s, 3H, –CH_3), 1.68–1.74 (m, 5H, –NCH_2CH_2–, –CH_3), 2.77 (s, 3H, –NCH_3), 4.16 (t, J=7.6 Hz, 2H, –NCH_2CH_2–), 7.05 (d, J=8.6 Hz, 1H, naph-H), 7.31 (t, J=7.4 Hz, 1H, naph-H), 7.46 (t, J=7.3 Hz, 1H, naph-H), 7.55 (t, J=8.1 Hz, 1H, naphthalimide-H), 7.84 (d, J=8.6 Hz, 1H, naph-H), 7.88 (d, J=8.3 Hz, 1H, naph-H), 7.93 (d, J=8.6 Hz, 2H, naph-H, naphthalimide-H), 8.25 (d, J=7.7 Hz, 1H, naphthalimide-H), 8.54 (d, J=6.5 Hz, 1H, naphthalimide-H), 8.70 (s, 1H, N=CH). ^{13}C NMR (500 MHz $CDCl_3$): 13.86, 20.41, 22.02, 24.00, 29.94, 30.26, 40.22, 54.05, 101.65, 110.15, 115.54, 121.22, 121.86, 122.39, 122.84, 124.60, 125.87, 126.42, 126.85, 128.12, 129.44, 129.70, 129.74, 129.80, 130.00, 131.99, 132.30, 144.91, 148.08, 153.06, 163.57, 164.22; HRMS (ESI) *m*/*z* calcd for $C_{32}H_{30}N_3O_3$: 504.2287 [M$^+$+H], found: 504.2261.

Acknowledgements

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