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Solution processable 2-(trityloxy)ethyl and *tert*-butyl group containing amorphous molecular glasses of pyranylidene derivatives with light-emitting and amplified spontaneous emission properties

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ABSTRACT

Small organic molecules with incorporated 4*H*-pyran-4-ylidene (pyranylidene) fragment as the π-conjugation system which bonds the electron acceptor fragment (A) with electron donor part (D) in the molecule – also well known as derivatives of 4-(dicyano-methylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran (**DCM**) laser dye-have attracted considerable attention of scientists as potential new generation materials for organic photonics and molecular electronics due to their low-cost fabrication possibility, flexibility and low-weight.

Six glassy derivatives of 4*H*-pyran-4-ylidene (pyranylidene) with attached bulky 2-(trityloxy)ethyl and *tert*-butyl groups are described in this report. Almost all of the synthesized compounds form good optical quality transparent amorphous films from volatile organic solvents and could be obtained in good yields up to 75%. Their light emission in solution and thin solid films is in the range of 600–700 nm, they are thermally stable and show glass transition in the range of 108–158 °C. The amplified spontaneous emission threshold values of the neat films of the glassy pyranylidene derivatives vary from 155 to 450 μJ/cm^2 and their HOMO and LUMO energy levels are between of those of tris(8-hydroxy quinolinato) aluminum (**Alq$_3$**). The photoluminescence quantum yields of the glassy compounds are in the range from 1% to about 7.7% and their electroluminescence properties have been investigated. Therefore, glassy pyranylidene derivatives could be a very potential low-cost solution processable materials for **Alq$_3$** hosted light-amplification and light-emitting application studies.

1. Introduction

D-π-A type organic molecules with the electron donating fragment bounded through π-conjugated system to the electron acceptor fragment in their structures have attracted considerable attention of scientists as potential materials for organic photonics and molecular electronics due to their low-cost fabrication possibility, flexibility and low-weight [1–3]. Among various kinds of such organic materials, one of the most notable organic luminophores contain 4*H*-pyran-4-ylidene (pyranylidene) as the π-conjugation system of the molecule [1,2,4–12]. They are also well known as derivatives of 4-(dicyano-methylene)-2-methyl-6-[p-(dimethylamino)styryl]-4*H*-pyran (**DCM**) laser dye [4,11,12] and could be used for OLED emission layer application studies [1,2,5–8,10], organic solid state lasers [1,4,11–13], logic gates [1,5], organic solar cells [1,14] and optical chemosensors [5].

One of the basic requirements for the organic compounds to be potential for light-emitting applications are: they have to be transparent with good optical quality and amorphous in their solid state [1–3]. Amorphous physical state of the organic compounds is known to be thermodynamically unstable and low molecular mass organic compounds could be obtained in it either by vacuum sublimation or in the result of a fast cooling [1,2]. With polymers such problems can be avoided as most of them form amorphous structure in their solid state, but their synthesis poses a repeatability challenge. Low molecular mass organic compounds can be synthesized with better repeatability than polymers or oligomers. Furthermore if small molecules could form amorphous phase by applying wet coating processes, it could be of great manufacturing advantage.

Previous researches [15,16] have showed that incorporation of bulky 2-(trityloxy)ethyl groups in low molecular mass organic

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compounds with 2,6-dimethyl-4*H*-pyran-4-ylidene fragment as backbone of the molecules results in formation of their amorphous glassy structure in the solid state from volatile organic solvents with glass transition (T_g) temperatures varying from 110 °C to 127 °C. Additionally, remarkable light-emission and amplified spontaneous emission properties were observed from their pure amorphous films [15,16] whereas similar physical properties were not detected from pure **DCM** films obtained by vacuum sublimation. Nevertheless such materials are hard to purify and separate due to *mono-* and *bis-* condensation product formation during the reaction. Additional drawback was, – that they were obtained in low yields [15]. Using 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one as a staring reactant not only could prevent the formation of *bis*-byproduct in the last stage of the material synthesis, but also make them obtainable in good yields. Six glassy 2-(trityloxy)ethyl group containing derivatives with 2-*tert*-butyl-6-methyl-4*H*-pyran-4-ylidene fragment as the backbone of the molecules are described in this work.

2. Experimental

All necessary reagents were purchased as commercial products from *Acros Organics*, *Sigma–Aldrich*, *Fisher Chemical* and *Alfa-Aesar*. Organic solvents (pyridine, dichloromethane, chloroform and piperidine) were dried by refluxing with calcium hydride and distilled. The ^{1}H NMR spectra were obtained on a Bruker UXNMR/XWIN-NMR spectrometer (300 MHz). Low-resolution mass spectra were acquired on a Waters EMD 1000 MS detector (ESI + mode, cone voltage 30 V). The element analysis of luminescent organic 4*H*-pyran-4-ylidene fragment containing derivatives were obtained with "Euro Vector 300" element analyzer.

2.1. Synthesis of compounds

2.1.1. 2-(tert-Butyl)-6-methyl-4H-pyran-4-one (4) [7]

To a stirred slurry of sodium hydride (3.0 g; 0.07 mol, 60 wt.%) in 1,2-dimethoxyethane (monoglyme; 50 mL) under argon atmosphere and at reflux temperature, was added a solution of acetylacetone (**1**) (2.5 g; 0.025 mol) in monoglyme (25 mL) followed, after 45 min, by a solution of methyl pivalate (**2**) (2.9 g; 0.025 mol) in monoglyme (25 mL). The reaction mixture was refluxed for 6 h. Most of the solvent was then removed by distillation under reduced pressure and the pasty residue was cooled to room temperature. Cold water (100 mL) and *tert*-butyl-methyl ether (MTB) (75 mL) were added, and the two layers formed were separated. The MTB layer was extracted with two portions of cold water (50 mL) and then with cold, 1% aqueous sodium hydroxide (50 mL). The extracts were combined with the original aqueous layer, and to the resulting aqueous solution hydrochloric acid (7–8 mL; 12 N) was added. The resulting slurry was extracted with four portions of MTB (75 mL). The ether extracts were combined and dried over anhydrous sodium sulfate. The solvent was evaporated to leave an oily residue (4.25 g). Without further characterization or further purification it was dissolved slowly in cold concentrated sulfuric acid (25 mL; 0 °C) and stirred for 1 h. After it was poured into cold water and neutralized with solid sodium bicarbonate. The resulting slurry was extracted with four portions of MTB (75 mL). The extracts were again combined and dried over anhydrous sodium sulfate. Removal of the MTB under reduced pressure left a brownish oily residue – 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one (**4**) (2.84 g; 69% yield based on acetylacetone or methyl pivalate).

2.1.2. General method of synthesis of compounds 6a–f

A solution of 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one (**4**) (1.64 g, 10.00 mmol) and respective active methylene group containing compound **A** (10.00 mmol) in acetic anhydride (5 mL) was stirred under reflux for 6 h, then left overnight to cool to the room temperature. Whenever possible – the formed solids were filtered and washed with cold methanol (20 mL), dried and used in synthesis without any further purification. In case no solid was formed, the reaction mixture was poured in distilled water (50 mL) and extracted with two portions of MTB (25 mL). The ether extracts were combined and dried over anhydrous sodium sulfate. After removing the ether under reduced pressure, the obtained dark brownish slurry was purified.

2.1.3. General method of synthesis of laser dyes *WK-1TB*

A solution of 4*H*-pyrane derivative **(6a–f)** (1.20 mmol), 4-(bis(2-(trityloxy)ethyl)amino)benzaldehyde **(7)** (0.82 g, 1.20 mmol) in dry pyridine (7 mL) was refluxed for 8 h. The reaction was controlled with thin layer chromatography (dichloromethane, silicagel). After no more corresponding 4*H*-pyrane derivative was found, the reaction solution was cooled to the room temperature and poured in ethanol (100 mL). Obtained solids were filtered and purified.

2.1.4. 2-(2-tert-Butyl-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (*6a*)

2-(2-*tert*-Butyl-6-methyl-4*H*-pyran-4-ylidene)-1*H*-indene-1,3(2*H*)-dione (**6a**) was synthesized by method described above and similar as described in [7,15] from 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one (**4**) (0.80 g, 4.80 mmol) and indene-1,3-dione (**5a**) (0.71 g, 4.80 mmol). After the purification of dark brownish slurry obtained in the reaction with a liquid column chromatography (dichloromethane, silicagel) a 0.35 g (23%) of 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-*tert*-butyl-4*H*-pyran-4-ylidene)-*1H*-indene-1,3(2*H*)-dione (**6a**) as yellow–greenish solid with m.p. 115 °C was obtained. ^{1}H NMR (300 MHz; DMSO-d_6) δ, ppm.: 1.32 (9H, s), 2.47 (3H, s), 7.71 (4H, m), 8.19 (1H, s), 8.39 (1H, s).

2.1.5. 2-(2-tert-Butyl-6-methyl-4H-pyran-4-ylidene)malononitrile (*6b*)

2-(2-*tert*-Butyl-6-methyl-4*H*-pyran-4-ylidene)malononitrile (**6b**) was synthesized by method described above and similar as described in [7,15] from 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one (**4**) (1.75 g, 10.70 mmol) and malononitrile (**5b**) (0.70 g, 10.70 mmol). After washing the dark yellow–orange solid obtained in the reaction with cold methanol (30 mL) a 2.11 g (64%) of 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-*tert*-butyl-4*H*-pyran-4-ylidene)malononitrile (**6b**) as yellow small solid needles with m.p. 135 °C was obtained. Compound **6b** could be further purified by recrystallization from methanol. ^{1}H NMR (300 MHz; DMSO-d_6) δ, ppm.: 1.27 (9H, s), 2.42 (3H, s), 6.50 (1H, s), 6.75 (1H, s).

2.1.6. 5-(2-tert-Butyl-6-methyl-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (*6c*)

5-(2-*tert*-Butyl-6-methyl-4*H*-pyran-4-ylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**6c**) was synthesized by method described above from 2-*tert*-butyl-6-methyl-4*H*-pyran-4-one (**4**) (1.43 g, 8.70 mmol) and pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5c**) (1.12 g, 8.70 mmol). After washing the dark yellow–orange solid obtained in the reaction with cold methanol (20 mL) a 1.71 g (71%) of 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-*tert*-butyl-4*H*-pyran-4-ylidene)-*1H*-indene-1,3(2*H*)-dione (**6c**) as yellow–orange solid with m.p. 251 °C was obtained. ^{1}H NMR (300 MHz; DMSO-d_6) δ, ppm.: 1.30 (9H, s), 2.46 (3H, s), 8.65 (1H, s), 8.88 (1H, s), 10.56 (1H, s), 11.12 (1H, s).