

HAPPY Dyes as Light Amplification Media in Thin Films

Elmars Zarins,* Julija Pervenecka, Elina Misina, Oleksandr Bezvikonnyi, Aivars Vembris, Karlis Balodis, Dmytro Volyniuk, Juozas V. Grazulevicius, and Valdis Kokars

Cite This: *J. Org. Chem.* 2021, 86, 3213–3222

Read Online

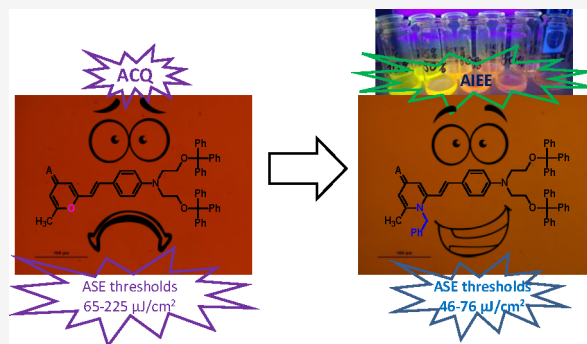
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: A series of 1*H* amorphous tri-phenyl pyridine (HAPPY) dyes have been synthesized from luminescent triphenyl-group-containing 2-methyl-6-styryl-substituted-4*H*-pyran-4-ylidene derivatives in reactions with benzylamine and investigated for suitability as solution-processable light-emitting medium components in thin films for amplified spontaneous emission (ASE). Conversion of a 4*H*-pyrane ring into a 1*H*-pyridine fragment enables aggregation-induced emission enhancement (AIEE) behavior in the target products and slightly increases thermal stability, glass transition temperatures, and ASE efficiency with PLQY up to 15% and ASE thresholds as low as 46 $\mu\text{J}/\text{cm}^2$ in neat spin-cast films, although thermal and photophysical properties are mostly dominated by the incorporated electron acceptors. Continued lasing parameter efficiency parameter improvement experiments revealed that no further optimization of HAPPY dyes by doping in polymer matrixes is required as the amplified spontaneous emission thresholds were lowest in pure neat films due to the AIEE phenomenon.



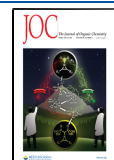
INTRODUCTION

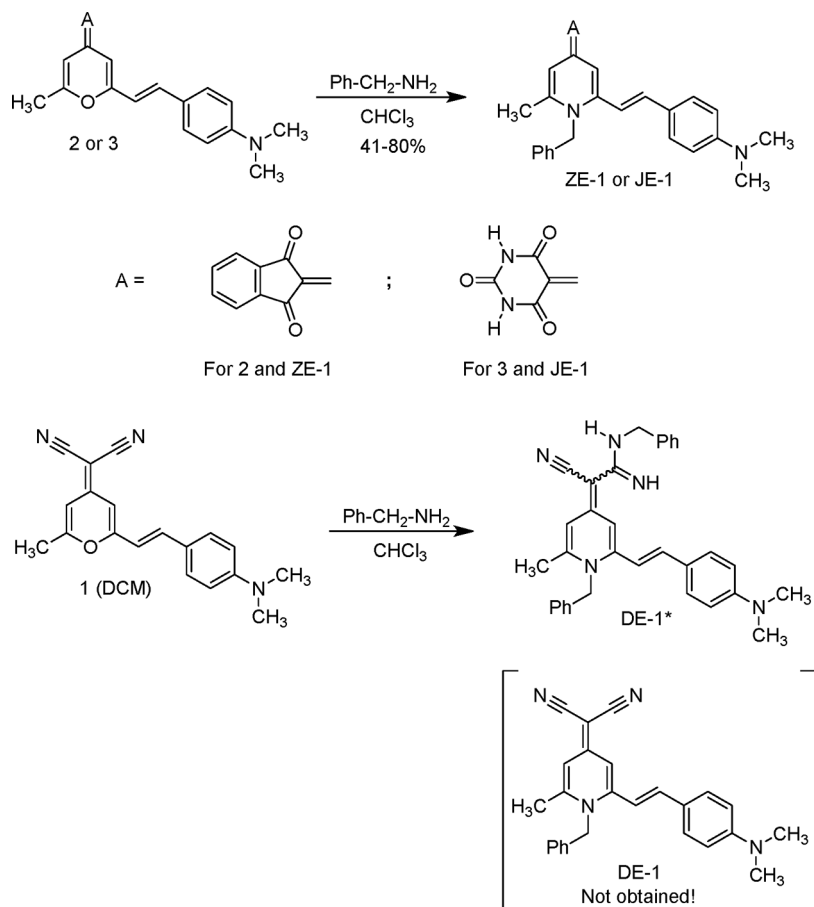
The demonstration of optical trapping and manipulation of neutral particles by lasers by A. Ashkin,¹ awarded a Nobel Prize in physics in 2018, opened new future perspectives for materials that can be used for laser radiation generation. Organic materials are good candidates to be applied as the gain medium components in lasers due to their low-cost production possibilities, good optical and photochemical stabilities, high optical quality of gain media, and a wide range of flexibility through chemical structure modifications.^{2–4} Among such materials, a typical gain medium system is composed of blends of aluminum tris(8-hydroxyquinoline) as a host and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM) as a guest.^{2–8} To increase the gain medium efficiency, the active lasing components can be doped in a matrix of a host,⁸ which can also be a polymer.⁹ The operation principle of lasing systems based on these materials is a Förster resonance energy transfer (FRET) from the excited host to the guest dye, which occurs due to the overlapping of their absorption and emission bands.^{2–8} The most notable advantages of this design are a significant reduction of reabsorption losses, low thresholds, and a remarkable increase in laser durability.^{2–4} Such gain media are usually produced by vacuum deposition,^{2–8} but several solution-processable system components also have been introduced.^{9,10} A number of various DCM derivatives were also synthesized and investigated for applications in communications, organic light-emitting diodes (OLED), nonlinear optics (NLO), and organic solar cells.¹¹ However, in all of those materials, 4*H*-pyran-4-ylidene fragment always remained unchanged.

The first conversion of 4*H*-pyran-4-ylidene-fragment-containing compounds into the respective 1*H*-pyridine-4-ylidene derivatives was reported by Kato et al.¹² in 1960. Nearly 30 years later, several synthesis possibilities of 2-(4-pyridinyl)indane-1,3-diones were described:¹³ (1) condensation of 4-methylpyridine with ethyl phthalates in the absence of catalyst; (2) oxidative condensation of *N*-alkylpyridinium bromides with indane-1,3-diones; (3) aminolysis of 2-(4*H*-pyran-4-ylidene) indane-1,3-diones, which was also the method reported previously by Kato.¹² In 2006, Peng et al.¹⁴ synthesized fluorescent polymers with incorporated 1*H*-pyridine-4-ylidene structural fragments. A detailed investigation of 4*H*-pyran-4-ylidene-fragment-containing compounds with primary and secondary amines¹⁵ and well-defined evidence of 1*H*-pyridine-4-ylidene derivative chemical structures by X-ray analysis were reported several years later.^{16–18} Recently, several 2,6-bis-styryl-substituted-1*H*-pyridine-4-ylidene derivatives were successfully synthesized and reported as materials with aggregation-induced emission enhancement (AIEE)¹⁹ and multicolor switching properties.^{18,20–23} Merocyanines are known for their prominent glass-forming and solid-state emission properties.²⁴ While many J-aggregates usually exhibit strong fluorescence, the

Received: October 29, 2020

Published: January 29, 2021



Scheme 1. Synthesis of 1*H*-Pyridine Model Compounds from Luminescent 4*H*-Pyran-4-ylidene Derivatives

examples of a merocyanine H-aggregate exhibiting well-resolved emission with a longer fluorescence lifetime relative to that of the monomer was reported recently,²⁵ proving the possibility of the usage of such kind of derivatives as materials exhibiting AIEE.²⁶ However, none of these compounds so far were reported as possible light amplification media.

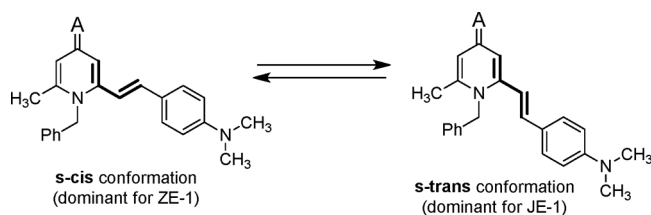
Herein we report the synthesis of 1*H* amorphous tri-phenyl pyridine (HAPPY) dyes from the respective luminescent triphenyl group containing 2-methyl-6-styryl-substituted-4*H*-pyran-4-ylidene derivatives. The results of the investigation of their thermal, glass-forming, light-emitting, and amplified spontaneous emission (ASE) properties in solution-processable thin films are described.

RESULTS AND DISCUSSION

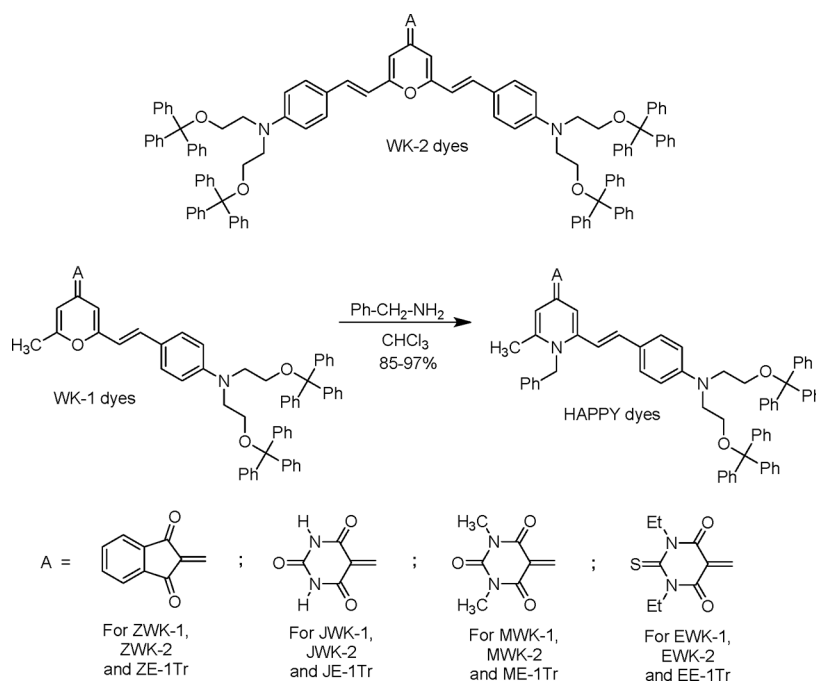
Synthesis of Dyes and Their Characterization. To test the conversion efficiency and to tune the reaction conditions for the donor (D)–acceptor (A) group containing 4*H*-pyran-4-ylidene derivative conversion into 1*H*-pyridine-fragment-containing compounds, several model compounds (1–3) have been synthesized as described previously.²⁸ Benzylamine was selected to increase the glass transition temperatures and enhance amorphous structure formation in the solid state of the desired target products. 1*H*-Pyridine-fragment-containing model compounds ZE-1 and JE-1 were successfully obtained (Scheme 1) by a slightly modified synthesis method reported by Kato et al.¹² from 4*H*-pyran-4-ylidene precursors 2 and 3. In contrast to the research reported previously,¹⁵ the reaction of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran

(DCM) with benzylamine did not afford the desired model compound DE-1 even in trace amounts. NMR and HPLC-MS analyses indicated successful 4*H*-pyran ring conversion into the 1*H*-pyridine fragment with the additional 1,2-addition of the benzylamine molecule to the malononitrile electron acceptor fragment affording compound DE-1* (see Supporting Information, pages S10–S16). No amine 1,2-additions to malononitrile acceptors were observed in literature^{14,15,21} with similar chemical structure 4*H*-pyran-4-ylidene-fragment-containing molecules and different reactants; however, in this research, those reaction conditions were not applied.

The chemical shifts in NMR spectra of model compounds ZE-1 and JE-1 NMR spectra are complex due to the close sterical interactions of benzyl and 4-(*N,N*-dimethylaminostyryl) fragments, which slow down rotations between different conformations (Scheme 2). Peaks from both conformers are

Scheme 2. Conformation Inversions of 1*H*-Pyridine Model Compounds ZE-1 and JE-1^a

^aA = the electron withdrawing substituent; see Scheme 1.

Scheme 3. Synthesis of HAPPY Dyes^a

^aBis-styryl-4H-pyran-4-ylidene derivatives ZWK-2, JWK-2, MWK-2, and EWK-2 (abbreviation used: WK-2 dyes) were obtained as byproducts in the synthesis of necessary reactants ZWK-1, JWK-1, MWK-1, and EWK-1 (abbreviation used: WK-1 dyes). Tr is the abbreviation of the triphenylmethane group.

observed at varying intensities and are dependent on the incorporated electron acceptor (see [Supporting Information](#), pages S23–S31). The hydrogen bond formation possibility between JE-1 molecules is most likely the reason why the S-trans conformation was dominant.

All HAPPY dyes were synthesized in a similar way like model compounds JE-1 and ZE-1 from the respective 4H-pyran-4-ylidene derivatives according to known procedures²⁴ and were obtained in high yields ([Scheme 3](#)). S-cis conformation was dominant for all of the synthesized HAPPY dyes (see [Supporting Information](#), pages S47–S70). The increased distance between the molecules of JE-1Tr due to the bulky groups most likely prevented possible aggregation through hydrogen bonds that enhances s-trans conformation in JE-1.

Thermal and Glass-Forming Properties. Thermal characteristics of synthesized HAPPY dyes as well as related reactants (WK-1 dyes) and their byproducts (WK-2 dyes) are summarized in [Table 1](#).

Compounds with free N–H groups (JWK-2, JWK-1, and JE-1Tr) show higher glass transition temperatures due to the hydrogen bond formation. No additional relations could be observed from the comparison of thermal characteristics of all investigated dyes (WK-1, WK-2, and HAPPY). It means that thermal stabilities and glass transition temperatures of the dyes are mostly influenced by the incorporated electron acceptor fragments. Conversion of a 4H-pyran ring into a 1H-pyridine fragment in reaction with benzylamine increased thermal stability and glass transition temperatures of ZE-1Tr, JE-1Tr, and ME-1Tr; however, the opposite regularity was observed for EE-1Tr. All of the investigated dyes showed thermal stability of 260 °C and above, good neat-film formation ability by solution-processing (see [Supporting Information](#), pages S79 and S80), and glass transition temperatures up to 140 °C. No definite melting points were observed for synthesized HAPPY dyes,

Table 1. Yields and Thermal Properties of WK-1, WK-2, and HAPPY Dyes^a

Compound	A	Yield, %	T _g , (°C)		T _d , (°C)	Reference
			1. heating	2. heating		
ZWK-2*		3	122	118	284	[21]
ZWK-1*		27	117	110	274	[21]
ZE-1Tr [†]		86	139	-	296	This work
JWK-2*		5	135	127	283	[21]
JWK-1*		8	133	120	266	[21]
JE-1Tr [†]		97	139	140	288	This work
MWK-2*		13	-	76	285	This work
MWK-1*		34	77	86	288	This work
ME-1Tr [†]		89	83	92	295	This work
EWK-2*		20	119	118	303	This work
EWK-1*		34	108	101	280	This work
EE-1Tr [†]		85	103	99	260	This work

^aT_g = glass transition temperature. T_d = thermal decomposition temperature at 5% weight loss. Symbols *, †, and [†] are used as identifiers for WK-1, WK-2, and HAPPY, respectively.

which additionally indicate the formation of amorphous structures in their solid state.

Photophysical Properties. A 10–30 nm redshift of absorption and photoluminescence bands of synthesized HAPPY dyes in neat films (see [Figure 2](#)) in relation to their dichloromethane solutions ([Figure 1](#)) indicates slight sensitivity of photophysical properties of compounds ZE-1Tr, JE-1Tr, ME-

1Tr, and EE-1Tr to the polarity of the surrounding solvation environment.

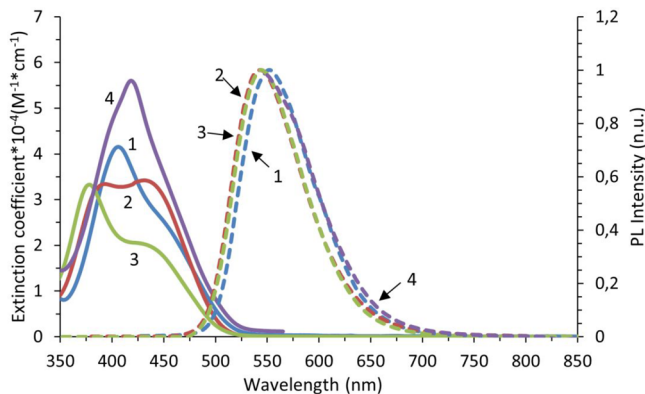


Figure 1. Absorption (solid lines) and photoluminescence (dashed lines) spectra of the solutions of HAPPY dyes in dichloromethane: 1, EE-1Tr; 2, ME-1Tr; 3, JE-1Tr; 4, ZE-1Tr.

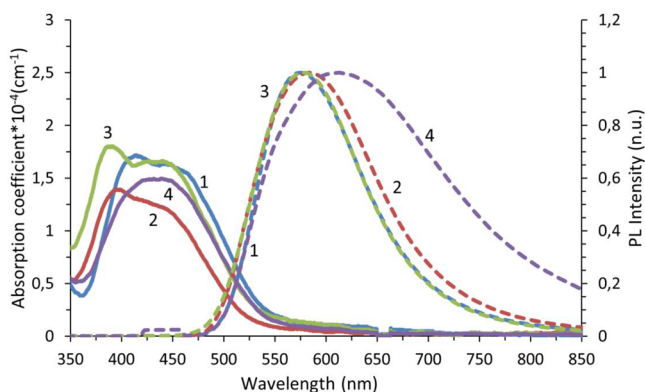


Figure 2. Absorption (solid lines) and photoluminescence (dashed lines) spectra of neat thin films of HAPPY dyes: 1, EE-1Tr; 2, ME-1Tr; 3, JE-1Tr; 4, ZE-1Tr.

The largest redshift was observed for ZE-1Tr bearing an indene-1,3(2H)-dione acceptor moiety. The conversion of a 4H-pyrene ring to a 1H-pyridine fragment had a significant influence on the photophysical properties in the solid state as the absorption and PL maxima of HAPPY dyes blueshifted by 54–130 nm (Table 2) in comparison to those of their respective precursors (WK-1 dyes). WK-2 dyes contain an additional electron donor fragment, which leads to an even greater redshift of their absorption and photoluminescence in relation to those of HAPPY dyes.

Distinct amplified spontaneous emission (ASE) was observed in three out of four HAPPY dye neat films (JE-1Tr, ME-1Tr, and EE-1Tr) (Table 2 and Figure 3), while only a small extra peak

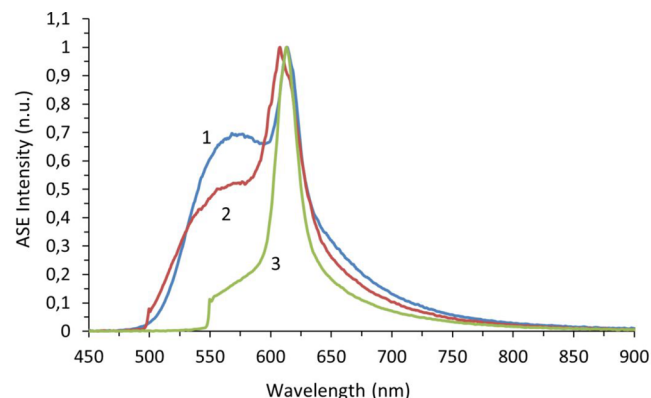


Figure 3. Amplified spontaneous emission of HAPPY dyes in pure thin films: 1, EE-1Tr; 2, ME-1Tr; 3, JE-1Tr.

appeared in the emission spectra of the ZE-1Tr film, which could be attributed to the phenomena. The respective precursor ZWK-1 also showed the lowest threshold energy among WK-1 dyes. It means that dyes with an indene-1,3(2H)-dione acceptor were the least effective as materials for light amplification. For an effective lasing parameter comparison of synthesized dyes, PLQY and ASE threshold energy should be evaluated together. Even though WK-1 dye neat films exhibit about 2 times higher PLQYs (in the case of JWK-1 → JE-1Tr and EWK-1 → EE-1Tr modifications), obtained HAPPY dyes still showed lower thresholds. Despite the largest overlap between the absorption

Table 2. Photophysical Properties of Pure Thin Films of WK-1, WK-2, and HAPPY Dyes in Pure Thin Films

compound	λ_{abs} , nm	λ_{PL} , nm	fwhm_{PL} , nm	PLQY, %	λ_{ASE} , nm	fwhm_{ASE} , nm	E_{th} , $\mu\text{J}/\text{cm}^2$	ref
ZWK-2 ⁺	519 ± 2	699; 827 ± 2	300 ± 2	1.2 ^M				24, 27
ZWK-1*	498 ± 2	668 ± 2	117 ± 2	10.7 ^M	699 ± 2	18 ± 2	225 ± 20	24, 27
ZE-1Tr [⋅])	431 ± 2	612 ± 2	208 ± 2	2.8	603 ± 2			this work
JWK-2 ⁺	499; 572 ± 2	717 ± 2	165 ± 2	6.1 ^M				24, 27
JWK-1*	514 ± 2	673 ± 2	122 ± 2	13.7 ^M	683 ± 2	15 ± 2	95 ± 10	24, 27
JE-1Tr [⋅])	386 ± 2	576 ± 2	143 ± 2	5.9	603 ± 2	19 ± 2	76.5 ± 7.6	this work
MWK-2 ⁺	501 ± 2	694 ± 2	135 ± 2	2.2	714 ± 2	16 ± 2	200.8 ± 20.1	this work
MWK-1*	491 ± 2	702 ± 2	143 ± 2	11.6	674 ± 2	20 ± 2	65.2 ± 6.5	this work
ME-1Tr [⋅])	395 ± 2	584 ± 2	157 ± 2	15.1	615 ± 2	23 ± 2	64.5 ± 6.4	this work
EWK-2 ⁺	525 ± 2	733 ± 2	145 ± 2	3.2	743 ± 2	16 ± 2	347.0 ± 34.7	this work
EWK-1*	523 ± 2	701 ± 2	158 ± 2	9.6	701 ± 2	21 ± 2	156.0 ± 15.6	this work
EE-1Tr [⋅])	413 ± 2	571 ± 2	119 ± 2	5.1	614 ± 2	12 ± 2	46.0 ± 4.6	this work

^a λ_{abs} : wavelength of absorption maximum. λ_{PL} : wavelength of photoluminescence maximum. PLQY: photoluminescence quantum yield. λ_{ASE} : wavelength of amplified spontaneous emission maximum. fwhm: the full width of half-maximum of PL or amplified spontaneous emission band. E_{th} : irradiation threshold energy density at which amplified spontaneous emission appears. Symbols *, +, and ⋅) are used as identifiers for WK-1, WK-2, and HAPPY, respectively. M: measured in spin-cast films that were about 10 times thinner than samples reported in ref 24.

and photoluminescence spectral regions, EE-1Tr has the lowest ASE excitation threshold energy value: $46 \mu\text{J}/\text{cm}^2$, which is approximately three times lower than the ASE excitation threshold value of its predecessor, EWK-1 (Figure 4).

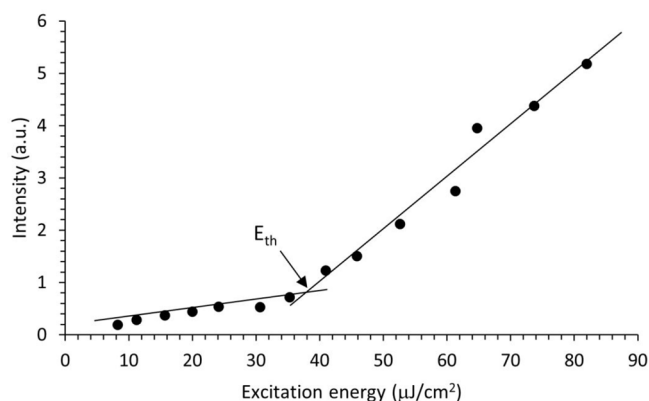


Figure 4. Emission intensity dependence on irradiation energy density in the EE-1Tr film.

Threshold energy densities of MWK-1 and ME-1Tr were nearly the same, but the PLQY was higher for ME-1Tr by about 1.3 times.

ASE properties of several WK-1 and WK-2 dyes were investigated as described,²⁷ and no such effect was observed in ZWK-2 and JWK-2 neat films. Surprisingly, the ASE effect was detected in MWK-2 and EWK-2 films in the infrared (IR) region. Even though PLQYs in MWK-2 and EWK-2 films were low and thresholds were relatively high, the efficiency of these materials is competitive with IR radiation amplifying compounds obtained previously.^{28,29} The 10 and 20 nm red shift of EWK-2 and MWK-2 ASE peaks from their photoluminescence maximum is in accordance with the theoretical statement that the cross section of the stimulated emission should be larger to the right side of the photoluminescence maximum.³⁰

Fluorescence lifetimes of all investigated dyes are below 1 ns (see Supporting Information, pages S89–S93). All of these results indicate that HAPPY dyes are more promising materials for light amplification in relation to WK-1 and WK-2 dyes, and the efficiency increase is mostly dependent on the incorporated electron acceptor fragment.

To improve the lasing efficiency parameters (PLQY and E_{th}) by increasing the distance and disabling interactions between molecules in the solid state, the three most efficient HAPPY dyes (JE-1Tr, ME-1Tr, and EE-1Tr) were doped in Zeonex³¹ matrix. PLQY increased only slightly (see Supporting Information, page S94); however, no ASE was observed at all in such host–guest systems. It may be due to two reasons: low solubility of the investigated HAPPY dye in Zeonex, which causes emitted light scattering instead of amplification and a small difference of refractive index between Zeonex and the glass substrate, which reduces the waveguide efficiency. Therefore a different polymer–polyvinylcarbazole (PVK) was used due to proven suitability in lasing systems.⁹ PLQY and ASE threshold energy dependence from doped dye ME-1Tr and EE-1Tr mass/weight concentrations (wt%) in PVK are shown in Figure 5. While a clear decrease of PLQY by increasing the dye content in PVK is clearly seen, no such trend could be established from ASE threshold energies. Even though low ASE thresholds are observed at 30 wt % dye ME-1Tr and EE-1Tr content in PVK

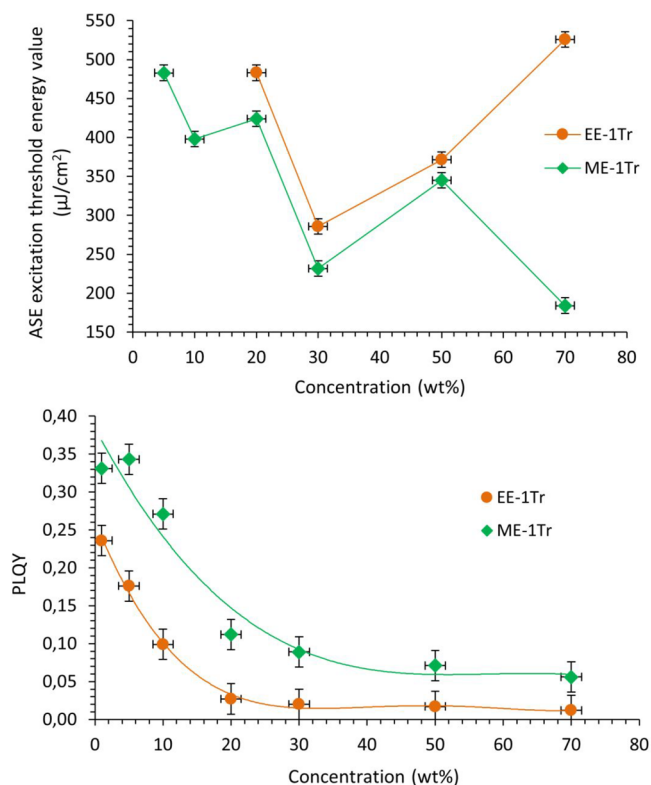


Figure 5. ASE threshold energy (top graph) and PLQY (bottom graph) in ME-1Tr and EE-1Tr dye-doped systems in PVK.

as well as at 70 wt % dye ME-1Tr content in PVK, the lowest values are still obtained in pure dye films despite a low PLQY (see Table 2). No ASE was observed in 1 wt % ME-1Tr and 1 wt %, 5 wt %, 10 wt % EE-1Tr dye-doped PVK films. Increasing dye ME-1Tr and EE-1Tr concentrations (wt%) in PVK caused a redshift of the PL maxima wavelength of the respective host–guest systems (see Supporting Information, pages S85–S87), like for 4*H*-pyran-4ylidene-fragment-containing reactants.^{9,32} However, increasing dye ME-1Tr and EE-1Tr concentrations (wt%) in PVK caused the blue shift of ASE maxima wavelengths (see Supporting Information, pages S85–S87), which was the exact opposite in comparison to reactant host–guest systems.^{9,31} Obtained results in PVK matrixes could be explained by a possible aggregation-induced emission enhancement (AIEE) phenomenon for HAPPY dyes in neat films.

As the PLQY of the solid films of the investigated HAPPY dyes were also higher than those of their deoxygenated toluene solutions (see Supporting Information, page S94), a classical experiment to test aggregation-induced emission properties was conducted (see Figure 6).

At 80–90% water content, a remarkable increase of PL intensity was observed for dye JE-1Tr and ME-1Tr samples. The reduction of PL intensity at 90–99% water content is apparently due to the uneven distribution of dye aggregates in a cuvette that leads to the emitted light scattering. The lowest-energy absorption bands of dilute THF solutions of all the compounds (see Figure 91S, page S97) observed at ca. 470 nm was slightly hypochromically shifted in comparison to the corresponding bands of the dispersions in the mixtures of THF and water with 99% volume fraction of water. The shift is caused by the different polarity of the media due to the different dielectric constants of water and THF, which are 80 and 7.5, respectively. The level-off tail was observed for the dispersions of the compounds at the

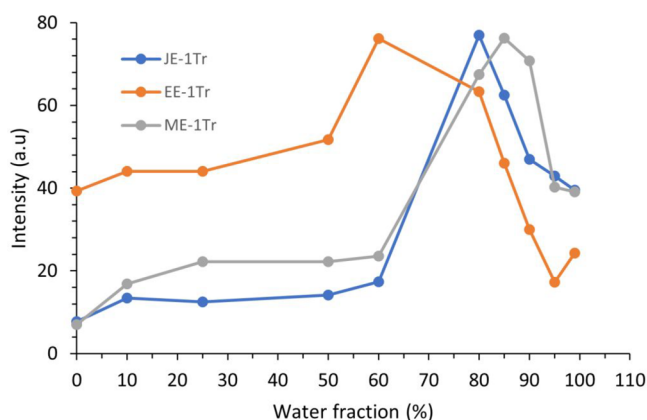


Figure 6. PL intensity versus water fraction for the dispersions of JE-1Tr, ME-1Tr, and EE-1Tr dyes in water/THF mixtures. In all samples, the molar concentration of dye was kept constant.

wavelengths exceeding 500 nm when the THF fraction was 1%. This observation indicates the formation of aggregates. Also, absorption of the dispersions was significantly suppressed when the water content was high. This observation can be attributed to the uneven distribution of the aggregates caused by the pure solubility of the compounds in water.

An increase of PL intensity at 60% water content in the case of EE-1Tr indicates AIEE at longer distances between molecules in comparison to ME-1Tr and JE-1Tr. At 80–99% water content, the PL intensity of EE-1Tr decreases rapidly. Possible explanations for such observations could be attributed to a gel-like solidification at higher concentrations—a phenomenon that was first observed by Scheibe et al.³³ as well as due to the additional aggregation quenching that starts to dominate at the closer distance between molecules. Also, the possibility of cis–trans isomerization shown in Scheme 2 has to be taken into account. The emissive behavior of dipolar merocyanine dyes was interpreted in terms of an energy barrier to a conical intersection. Nonradiative deactivation of excitation can be characterized by a return to the reactant minimum or cis–trans isomerization in polar medium.³⁴ Nevertheless, all three investigated HAPPY dyes (JE-1Tr, ME-1Tr, and EE-1Tr) showed AIEE behavior, which could affect the increased light amplification efficiency in neat films.

CONCLUSIONS

Organic donor–acceptor dyes with a 1H-pyridine fragment as the backbone of the molecule and π -conjugation system can be conveniently synthesized from the relevant 4H-pyran-4-ylidene fragment containing luminophores in a one-step reaction with benzyl-amine and obtained in high yields. However, such synthesis is unsuccessful if a malononitrile electron acceptor is used. Conversion of the 4H-pyran-4-ylidene backbone into a 1H-pyridine fragment enables AIEE behavior of the dyes and slightly increases thermal stability, glass transition temperatures, and lasing efficiency in most cases. Thermal and photophysical properties of the synthesized materials were mostly dependent on incorporated electron acceptors: dyes with 1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione and 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione fragments showed the highest efficiency as light amplifiers (with PLQY up to 15% and ASE thresholds as low as 46 $\mu\text{J}/\text{cm}^2$ for neat films), while compounds with the 1H-indene-1,3(2H)-dione group were least efficient. Doping the dyes in the PVK matrix resulted in the increased

PLQY several times; however, ASE thresholds were still the lowest for pure neat films. This observation shows that no further optimization by doping of laser dyes with AIEE is required as the most efficient light amplification parameters are achieved for pure films. Similar results may also be obtainable for other organic molecules exhibiting ASE and AIEE properties.

EXPERIMENTAL SECTION

Unless specifically stated otherwise, all reactions were performed under ambient conditions. Starting reagents necessary for the synthesis of dyes were purchased as commercial products from Acros Organics, Sigma-Aldrich, Fisher Chemical, and Alfa-Aesar and used as received. Where required, organic solvents and catalysts (pyridine, piperidine, dichloromethane, chloroform, triethylamine) were dried by refluxing with calcium hydride (or phosphorus pentoxide) and distilled. The ^1H NMR spectra were obtained on a Bruker AVANCE spectrometer, 300 MHz at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants, J , are given in hertz (Hz). NOESY spectra of 1H-pyridine model compounds were acquired on a Bruker AVANCE spectrometer, 500 MHz at 298 K. The elemental analyses were obtained with an Euro Vector EA 300 element analyzer. The purity and the ratio of conformers were analyzed with Waters Alliance 2695 HPLC equipped with an XTerra MS C18 5 μm 2.1 mm $\times$ 100 mm column (0.2 mL/min flow), Waters 2996 PDA detector (250–800 nm), and Waters EMD 1000 (ESI) mass spectrometer (cone voltage = 30 V). Gradient elution was used (0.5% HCOOH buffer in deionized water, MeCN, and CH_2Cl_2). The detector is unable to register m/z peaks higher than 1080. Detailed information about structure characterization (^1H NMR spectra and HPLC-MS analysis) and physical properties of every chemical substance obtained in this article is available within the associated Supporting Information. Synthesized WK-1 dyes (ZWK-1, JWK-1, MWK-1, and EWK-1) and WK-2 dyes (ZWK-2, JWK-2, MWK-2, and EWK-2) are partly amorphous. Therefore, their melting points are not a definite way of characterization as those may vary depending on the content of the amorphous and crystalline forms in the synthesized batch.

General Method I: Synthesis of 1H-Pyridine Model Compounds and HAPPY Dyes. To a solution of the corresponding 2-styryl-substituted-6-methyl-4H-pyran-4-ylidene derivative (0.45 mmol) in chloroform (10 mL) was added a large excess (20.4 equiv) of benzylamine (1.0 mL, 9.16 mmol). The reaction mixture was refluxed for 3 h on an oil bath and then cooled to room temperature. After the solvent was removed under reduced pressure, ethanol (20 mL) was added to the obtained slurry, and the suspension was stirred for 1 h at room temperature. Afforded precipitates were filtered, washed with cold methanol (10 mL), dried, and then characterized as obtained. Some compounds were also further purified.

2-(1-Benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione (ZE-1) was synthesized by general method I from 2-(2-(4-(dimethylamino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (**2**) (0.18 g, 0.470 mmol) and about 20 equiv of benzylamine (1.0 mL, 9.16 mmol). After the required workup, 0.09 g (40.5%) of 2-(1-benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione (ZE-1) as a yellow-orange powder with an mp of 175 $^\circ\text{C}$ was obtained. IR (paraffin oil) ν , cm^{-1} : 3086, 3066, 3029, 2982, 2944, 2901, 2867, 2811, 1677, 1659, 1627, 1604, 1506, 1464. ^1H NMR (CDCl_3 , 300 MHz): δ 9.14 (s, 1H, major conformer), 8.84 (s, 1H, minor conformer), 8.78 (s, 1H, minor conformer), 8.71 (s, 1H, major conformer), 7.65–7.61 (m, 2H), 7.52–7.46 (m, 2H), 7.45–7.27 (m, 5H), 7.09–6.90 (m, 3H, major conformer), 6.69–6.41 (m, 3H), 6.06–6.00 (d, 1H, J = 12.1 Hz, minor conformer), 5.37 (s, 2H, major conformer), 5.33 (s, 2H, minor conformer), 3.00 (s, 6H, major conformer), 2.94 (s, 6H, minor conformer), 2.48 (s, 3H, major conformer), 2.47 (s, 3H, minor conformer). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz): δ 193.0, 151.3, 150.9, 149.9, 148.3, 140.4, 140.3, 131.8, 129.6, 129.1, 128.4, 125.2, 119.9, 116.5, 113.7, 111.9, 102.9, 52.78, 40.2, 21.0. Anal. Calcd for

C32H28O2N2: C, 81.33; H, 5.97; N, 5.93. Found: C, 81.15; H, 5.99; N, 6.02.

5-(1-Benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (JE-1) was synthesized by [general method I](#) from 5-(2-(4-(dimethylamino)styryl)-6-methyl-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (3) (0.16 g, 0.438 mmol) and about 20 equiv of benzylamine (1.0 mL, 9.16 mmol). After the required workup, 0.16 g (80%) of 5-(1-benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (JE-1) as a dark-yellow powder with an mp > 300 °C (dec.) was obtained. IR (paraffin oil) ν , cm⁻¹: 3136, 3083, 2956, 2921, 2851, 2804, 1715, 1687, 1663, 1587, 1532, 1463, 1414. ¹H NMR (CDCl₃, 300 MHz): δ 9.37 (s, 1H, minor conformer), 9.11 (s, 1H, major conformer), 9.05 (s, 1H, major conformer), 8.97 (s, 1H, minor conformer), 7.45–7.34 (m, 5H), 7.08–7.04 (d, 2H, *J* = 8.0 Hz, minor conformer), 7.01–6.90 (m, 4H, major conformer), 6.75–6.70 (d, 1H, *J* = 12.4 Hz, major conformer), 6.11–6.05 (d, 1H, *J* = 12.1 Hz, major conformer), 5.46 (s, 2H, minor conformer), 5.43 (s, 2H, major conformer), 3.02 (s, 6H, minor conformer), 2.99 (s, 6H, major conformer), 2.55 (s, 3H, minor conformer), 2.54 (s, 3H, major conformer). ¹³C{¹H} NMR (DMSO-*d*₆, 300 MHz): δ 165.7, 165.6, 153.9, 151.7, 150.8, 150.7, 150.3, 149.4, 139.5, 137.0, 135.8, 135.2, 130.8, 129.6, 128.2, 126.1, 123.3, 122.1, 120.0, 119.5, 116.2, 115.1, 112.3, 112.1, 87.8, 52.7, 21.6. Anal. Calcd for C₂₇H₂₆O₄N₄: C, 71.35; H, 5.77; N, 12.33. Found: C, 71.35; H, 5.77; N, 12.33.

Attempted synthesis of 1-benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene-malononitrile (DE-1) was carried out by [general method I](#) from 2-(4-(dimethylamino)styryl)-6-methyl-4H-pyran-4-ylidene-malononitrile (1) (0.21 g, 0.693 mmol) and about 20 equiv of benzylamine (1.0 mL, 9.16 mmol). After the required workup, 0.13 g (38%) of N-benzyl-2-(1-benzyl-2-(4-(dimethylamino)styryl)-6-methylpyridin-4(1H)-ylidene)-2-cyanoacetimidamide (DE-1*) as a yellow amorphous powder with an mp of 209 °C was obtained. ¹H NMR (CDCl₃, 300 MHz): δ 11.19 (s, 1H), 7.57 (d, 1H, *J* = 15.6 Hz), 7.40 (d, 4H, *J* = 7.8 Hz), 7.31–7.09 (m, 10H), 6.76 (d, 1H, *J* = 15.7 Hz), 6.65 (d, 2H, *J* = 8.5 Hz), 6.23 (s, 1H), 5.83 (s, 1H), 4.90 (s, 2H), 4.81 (s, 2H), 2.93 (s, 6H), 2.19 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 300 MHz): δ 157.6, 157.0, 155.2, 150.4, 143.6, 135.1, 133.2, 129.3, 128.4, 128.3, 127.8, 127.7, 126.5, 125.4, 124.1, 112.4, 105.2, 104.1, 103.5, 48.3, 45.2, 40.4, 21.3. Anal. Calcd for C₃₃H₃₃N₅: C, 79.33; H, 6.66; N, 14.02. Found: C, 78.98; H, 6.62; N, 13.70.

2-(1-Benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione (ZE-1Tr) was synthesized by [general method I](#) from 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK-1)²⁴ (0.10 g, 0.11 mmol) and benzylamine (0.5 mL, 4.08 mmol). After the required workup, 0.10 g (86.4%) of 2-(1-benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1H-indene-1,3(2H)-dione (ZE-1Tr) as an orange amorphous powder was obtained. IR (paraffin oil) ν , cm⁻¹: 3088, 3060, 3024, 2921, 2851, 1673, 1661, 1629, 1592, 1580, 1532, 1521, 1504, 1463, 1456. ¹H NMR (CDCl₃, 300 MHz): δ 9.09 (s, 1H, major conformer), 8.80 (s, 1H, minor conformer), 8.74 (s, 1H, minor conformer), 8.66 (s, 1H, major conformer), 7.62–7.55 (m, 2H), 7.46–7.41 (m, 2H), 7.39–6.99 (m, 40H), 6.81 (d, 2H, *J* = 7.8 Hz, major conformer), 6.56 (s, 1H, *J* = 12.6 Hz, minor conformer), 6.49 (s, 1H, *J* = 15.6 Hz, major conformer), 6.37 (d, 2H, *J* = 8.6 Hz, major conformer), 6.29 (d, 2H, *J* = 8.5 Hz), 5.91 (d, 1H, *J* = 12.4 Hz, minor conformer), 5.31 (s, 2H, major conformer), 5.17 (s, 2H, minor conformer), 3.56–3.41 (m, 4H), 3.26–3.14 (m, 4H), 2.43 (s, 3H, major conformer), 2.30 (s, 3H, minor conformer). ¹³C{¹H} NMR (CDCl₃, 300 MHz): δ 186.1, 183.6, 143.9, 140.4, 128.6, 127.9, 127.8, 127.0, 110.6, 102.7, 66.6, 64.3, 61.0, 60.8, 21.0. Anal. Calcd for C₇₂H₆₀O₄N₂: C, 85.01; H, 5.95; N, 2.75. Found: C, 84.75; H, 6.09; N, 3.06.

5-(1-Benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (JE-1Tr) was synthesized by [general method I](#) from 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (JWK-1)²⁴ (0.16 g, 0.17 mmol) and benzylamine (0.8 mL, 7.32 mmol). After the required workup, 0.17 g (96.8%) of 5-

(1-benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (JE-1Tr) as an orange amorphous powder was obtained. IR (paraffin oil) ν , cm⁻¹: 3425, 3386, 3168, 3083, 3058, 3025, 2966, 2925, 2877, 2813, 1706, 1657, 1614, 1588, 1526, 1464. ¹H NMR (CDCl₃, 300 MHz): δ 9.36 (s, 1H, major conformer), 9.36 (s, 1H, major conformer), 9.13 (s, 1H, minor conformer), 9.06 (s, 1H, minor conformer), 8.95 (s, 1H, major conformer), 7.69–7.03 (m, 44H), 6.86–6.77 (m, 2H, minor conformer), 6.64 (d, 1H, *J* = 12.4 Hz, minor conformer), 6.57 (d, 1H, *J* = 15.6 Hz, major conformer), 6.44 (d, 2H, *J* = 8.7 Hz, major conformer), 6.37 (d, 2H, *J* = 8.9 Hz, minor conformer), 5.43 (s, 2H, major conformer), 5.29 (s, 2H, minor conformer), 3.57 (s, 4H), 3.26 (s, 4H), 2.53 (s, 3H, major conformer), 2.40 (s, 3H, minor conformer). ¹³C{¹H} NMR (CDCl₃, 300 MHz): δ 165.1, 143.9, 141.3, 129.8, 129.4, 128.6, 127.8, 127.0, 125.2, 122.6, 118.0, 116.9, 112.6, 111.6, 112.6, 111.6, 104.3, 87.1, 70.0, 61.0, 51.0, 21.1. Anal. Calcd for C₆₇H₅₈O₅N₄: C, 80.54; H, 5.85; N, 5.85. Found: C, 80.29; H, 5.94; N, 5.69.

5-(1-Benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (ME-1Tr) was synthesized by [general method I](#) from 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (MWK-1) (0.27 g, 0.27 mmol) and benzylamine (1.0 mL, 9.16 mmol). After the required workup and additional purification by liquid column chromatography (silica gel, V(triethylamine)/V(ethyl acetate)/V(dichloromethane) = 1:10:40 solvent system), 0.25 g (89%) of 5-(1-benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (ME-1Tr) as a yellow amorphous powder was obtained. IR (paraffin oil) ν , cm⁻¹: 3079, 3059, 3027, 2964, 2924, 2882, 1696, 1688, 1623, 1601, 1589, 1520, 1479, 1462, 1406. ¹H NMR (CDCl₃, 300 MHz): δ 9.37 (s, 1H, major conformer), 9.17 (s, 1H, minor conformer), 9.11 (s, 1H, minor conformer), 9.00 (s, 1H, major conformer), 7.47–7.01 (m, 42H), 6.86–6.78 (m, 1H, mixture of conformers), 6.64–6.52 (m, 2H, mixture of conformers), 6.43 (d, 2H, *J* = 8.5 Hz, major conformer), 6.35 (d, 2H, *J* = 8.9 Hz, minor conformer), 6.05 (d, 1H, *J* = 12.7 Hz, minor conformer), 5.42 (s, 2H, major conformer), 5.27 (s, 2H, minor conformer), 3.56 (s, 4H), 3.41 (s, 6H, major conformer), 3.36 (s, 6H, minor conformer), 3.26 (s, 4H), 2.51 (s, 3H, major conformer), 2.39 (s, 3H, minor conformer). ¹³C{¹H} NMR (CDCl₃, 300 MHz): δ 164.4, 155.4, 152.4, 150.4, 149.2, 147.6, 143.9, 140.8, 133.5, 129.7, 129.2, 128.6, 127.8, 127.0, 121.2, 118.4, 113.1, 111.5, 89.6, 87.1, 61.1, 53.2, 51.0, 27.9, 21.2. Anal. Calcd for C₆₉H₆₂O₅N₄: C, 80.68; H, 6.08; N, 5.45. Found: C, 80.44; H, 6.15; N, 5.52.

5-(1-Benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (EE-1Tr) was synthesized by [general method I](#) from 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (EWK-1) (0.17 g, 0.17 mmol) and benzylamine (1.0 mL, 9.16 mmol). After the required workup and additional purification by liquid column chromatography (silica gel, V(triethylamine)/V(ethyl acetate)/V(dichloromethane) = 1:10:40 solvent system), 0.09 g (85%) of 5-(1-benzyl-2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methylpyridin-4(1H)-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (EE-1Tr) as an orange amorphous powder was obtained. IR (paraffin oil) ν , cm⁻¹: 3650, 3459, 3051, 3029, 3022, 2987, 2970, 2950, 2929, 2867, 1738, 1728, 1656, 1651, 1619, 1586, 1554, 1521, 1481, 1448, 1420. ¹H NMR (CDCl₃, 300 MHz): δ 9.31 (s, 1H, major conformer), 9.17 (s, 1H, minor conformer), 9.11 (s, 1H, minor conformer), 8.95 (s, 1H, major conformer), 7.47–7.01 (m, 41H), 6.85–6.76 (m, 2H, mixture of conformers), 6.64 (d, 1H, *J* = 12.4 Hz, minor conformer), 6.57 (d, 1H, *J* = 15.7 Hz, major conformer), 6.45 (d, 2H, *J* = 8.8 Hz, major conformer), 6.36 (d, 2H, *J* = 9.0 Hz, minor conformer), 6.06 (d, 1H, *J* = 12.0 Hz, minor conformer), 5.44 (s, 2H, major conformer), 5.30 (s, 2H, minor conformer), 4.75–4.59 (m, 4H), 3.55 (m, 4H), 3.26 (m, 4H), 2.54 (s, 3H, major conformer), 2.42 (s, 3H, minor conformer), 1.42–1.27 (m, 6H). ¹³C{¹H} NMR (CDCl₃, 300 MHz): δ 177.0, 162.1, 155.4, 150.8, 149.4, 147.9, 143.9, 141.3, 133.2, 129.8, 129.4, 128.6, 127.8, 127.0, 125.2, 119.6, 112.7, 111.6, 87.00, 61.1,

53.5, 51.0, 43.2, 21.2, 12.8. Anal. Calcd for $C_{71}H_{66}O_4N_4S$: C, 79.60; H, 6.21; N, 5.23. Found: C, 79.35; H, 6.30; N, 5.36.

General Method II: Synthesis of 4H-Pyranes 8a–d.²⁴ A solution of 2,6-dimethyl-4H-pyran-4-one (7)^{24,35} (10.0 mmol) and the corresponding active methylene group containing compound A (10.0 mmol) in acetic anhydride (5.0 mL) was stirred for 3 h at 110–120 °C on an oil bath and then left overnight to cool to room temperature. The formed solids were filtered off, washed with cold methanol (20 mL), and then dried. Obtained products were characterized and used in the next steps of synthesis without further purification.

2-(2,6-Dimethyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (8a), 5-(2,6-dimethyl-4H-pyran-4-ylidene)pyrimidine-2,4,6-(1H,3H,5H)-trione (8b), 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (8c), and 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (8d) were synthesized by general method II, according to known literature sources.^{23,35–40}

General Method III: Synthesis of Triphenyl Groups Containing 4H-Pyran-4-ylidene (WK-1 and WK-2) Dyes.²⁴ To a solution of the corresponding (2,6-dimethyl-4H-pyran-4-ylidene) derivative (8a, 8b, 8c, or 8d) (1.00 mmol) and 4-(bis(2-(trityloxy)ethyl)amino)-benzaldehyde (9) (1.00 mmol) in dry pyridine (5.0 mL) 3 drops of piperidine were added. The reaction mixture was stirred for 8 h at 90–100 °C on an oil bath, then cooled to room temperature. The obtained brownish slurry was poured into 100 mL of ethyl alcohol, and the afforded precipitates were filtered, washed with 10 mL of cold methanol, and dried. The obtained *mono*- (ZWK-1, JWK-1, MWK-1, and MWK-1 = abbreviated as WK-1 dyes) and *bis*- (ZWK-2, JWK-2, MWK-2, and EWK-2 = abbreviated as WK-2 dyes) condensation products were separated by a flash column chromatography.

2-(2-(4-(Bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK-1) and 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-(4-(1,5-bis(trityloxy)pentan-3-yl)-styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK-2) as well as 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)pyrimidine-2,4,6-(1H,3H,5H)-trione (JWK-1) and 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-(4-(1,5-bis(trityloxy)pentan-3-yl)-styryl)-4H-pyran-4-ylidene)pyrimidine-2,4,6-(1H,3H,5H)-trione (JWK-2) were synthesized by general method III, according to the literature.²⁴

5-(2-(4-(Bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (MWK-1) and 5-(2,6-bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (MWK-2) were synthesized by general method III from 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (8c) (0.25 g, 0.94 mmol) and 4-(bis(2-(trityloxy)ethyl)amino)-benzaldehyde (9) (0.63 g, 0.94 mmol). After separation and purification by flash column chromatography (silica gel, V-(dichloromethane)/V(ethyl acetate) = 12:1 solvent system), 0.30 g (34%) of 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (MWK-1) as an orange amorphous powder with an mp of 149 °C was obtained. IR (paraffin oil) ν , cm^{-1} : 3458, 3080, 3056, 3023, 2990, 2970, 2953, 2928, 2881, 2475, 2337, 1737, 1705, 1649, 1637, 1631, 1598, 1529, 1472, 1448, 1429, 1408. ¹H NMR ($CDCl_3$, 300 MHz): δ 8.89 (s, 1H), 8.70 (s, 1H), 7.45–7.10 (m, 33H), 6.61 (d, 1H, J = 15.9 Hz), 6.51 (d, 2H, J = 8.7 Hz), 3.58 (t, 4H, J = 5.4 Hz), 3.36 (s, 6H), 3.30 (t, 4H, J = 5.3 Hz), 2.47 (m, 3H). ¹³C{¹H} NMR ($CDCl_3$, 300 MHz): δ 163.4, 163.1, 157.1, 151.7, 149.7, 143.9, 138.2, 129.7, 128.6, 127.8, 127.1, 122.5, 114.0, 111.8, 110.9, 110.5, 87.1, 61.0, 51.1, 28.1, 20.7. Anal. Calcd for $C_{62}H_{55}O_6N_3$: C, 79.38; H, 5.91; N, 4.48. Found: C, 79.15; H, 6.14; N, 4.48.

After flash column chromatography, 0.39 g (27%) of 5-(2,6-bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1H,3H,5H)-trione (MWK-2) as a dark-violet amorphous powder with an mp of 142 °C was also obtained. IR (paraffin oil) ν , cm^{-1} : 3628, 3493, 3056, 3036, 3025, 2970, 2951, 2941, 2919, 2865, 2343, 1737, 1703, 1643, 1630, 1591, 1555, 1520, 1491,

1456, 1448, 1428, 1456, 1448, 1428, 1401. ¹H NMR ($CDCl_3$, 300 MHz): δ 8.89 (s, 2H), 7.50–7.10 (m, 66H), 6.71 (s, 2H, J = 15.9 Hz), 6.59 (d, 4H, J = 8.6 Hz), 3.66 (m, 8H), 3.42 (s, 6H), 3.36 (m, 8H). ¹³C{¹H} NMR ($CDCl_3$, 300 MHz): δ 164.3, 161.6, 156.6, 151.8, 149.6, 143.9, 137.6, 129.6, 128.6, 127.9, 127.1, 114.7, 111.8, 111.2, 87.1, 61.0, 51.1, 28.0. Anal. Calcd for $C_{111}H_{96}O_8N_4$: C, 82.60; H, 6.00; N, 3.47. Found: C, 82.27; H, 6.05; N, 3.60.

5-(2-(4-(Bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (EWK-1) and 5-(2,6-bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (EWK-2) were synthesized by general method III from 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (8d) (0.25 g, 0.81 mmol) and 4-(bis(2-(trityloxy)ethyl)amino)benzaldehyde (9) (0.55 g, 0.81 mmol). After separation and purification by flash column chromatography (silica gel, V(dichloromethane)/V(ethyl acetate) = 10:1 solvent system), 0.27 g (34%) of 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (EWK-1) as a dark-red amorphous powder with an mp of 130 °C was obtained. IR (paraffin oil) ν , cm^{-1} : 3508, 3056, 3024, 2978, 2972, 2928, 2908, 2879, 2474, 2323, 1736, 1668, 1630, 1609, 1593, 1553, 1525, 1490, 1464, 1447, 1440, 1430, 1402. ¹H NMR ($CDCl_3$, 300 MHz): δ 8.94 (s, 1H), 8.74 (s, 1H), 7.50–7.10 (m, 33H), 6.67 (d, 1H, J = 15.8 Hz), 6.56 (d, 2H, J = 8.5 Hz), 4.64 (q, 4H, J = 6.6 Hz), 3.63 (m, 4H), 3.34 (m, 4H), 2.54 (s, 3H), 1.36 (t, 6H, J = 6.6 Hz). ¹³C{¹H} NMR ($CDCl_3$, 300 MHz): δ 162.6, 159.7, 143.9, 129.7, 128.6, 127.9, 127.3, 127.0, 124.9, 43.4, 20.8, 12.6. Anal. Calcd for $C_{64}H_{59}O_5N_3S$: C, 78.26; H, 6.05; N, 4.28. Found: C, 78.07; H, 6.25; N, 4.29.

After flash column chromatography, 0.40 g (30%) of 5-(2,6-bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1H,5H)-dione (EWK-2) as a dark-violet amorphous powder with an mp of 140 °C was also obtained. IR (paraffin oil) ν , cm^{-1} : 3609, 3459, 3056, 3032, 3024, 2970, 2926, 2894, 2877, 2446, 2325, 1741, 1718, 1662, 1630, 1584, 1560, 1519, 1490, 1454, 1446, 1429. ¹H NMR ($CDCl_3$, 300 MHz): δ 8.91 (s, 2H), 7.50–7.10 (m, 66H), 6.72 (d, 2H, J = 15.8 Hz), 6.62 (d, 4H, J = 8.4 Hz), 4.70 (q, 4H, J = 6.6 Hz), 3.69 (m, 8H), 3.40 (m, 8H), 1.46 (t, 6H, J = 6.6 Hz). ¹³C{¹H} NMR ($CDCl_3$, 300 MHz): δ 177.4, 162.0, 157.2, 149.8, 143.9, 129.8, 128.6, 127.9, 127.1, 122.7, 144.4, 112.2, 96.0, 87.2, 61.0, 51.1, 43.4, 12.7. Anal. Calcd for $C_{113}H_{100}O_7N_4S$: C, 81.85; H, 6.08; N, 3.38. Found: C, 81.72; H, 6.13; N, 3.53.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.0c02574>.

Structure characterization data of reactants and investigated substances; detailed thermal, optical, and photophysical characterization experimental details (PDF)

FAIR data, including the primary NMR FID files, for compounds ZE-1, JE-1, DE-1*, MWK-1, MWK-2, EWK-1, EWK-2, ZE-1Tr, JE-1Tr, ME-1Tr, and EE-1Tr (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

Elmars Zarins – Institute of Applied Chemistry, Riga Technical University, Riga LV-1048, Latvia; Institute of Solid State Physics, University of Latvia, Riga LV-1063, Latvia;

orcid.org/0000-0002-5103-7511;

Email: Elmars.Zarins@rtu.lv

Authors

Julija Pervenecka – Institute of Solid State Physics, University of Latvia, Riga LV-1063, Latvia

Elina Misina – Institute of Applied Chemistry, Riga Technical University, Riga LV-1048, Latvia

Oleksandr Bezvikonnyi – Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas 51423, Lithuania

Aivars Vembris – Institute of Solid State Physics, University of Latvia, Riga LV-1063, Latvia

Karlis Balodis – Institute of Applied Chemistry, Riga Technical University, Riga LV-1048, Latvia

Dmytro Volyniuk – Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas 51423, Lithuania; orcid.org/0000-0003-3526-2679

Juozas V. Grazulevicius – Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas 51423, Lithuania; orcid.org/0000-0002-4408-9727

Valdis Kokars – Institute of Applied Chemistry, Riga Technical University, Riga LV-1048, Latvia

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.joc.0c02574>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. E.Z. and J.P. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the European Regional Development Fund within the Activity 1.1.1.2 “Post-doctoral Research Aid” of the Specific Aid Objective 1.1.1 “To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure” of the Operational Program “Growth and Employment” (1.1.1.2/VIAA/1/16/035). This work was also partially supported by European Union’s Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie grant agreement no. 823720. The Institute of Solid State Physics at the University of Latvia as the Center of Excellence has received funding from the European Union’s Horizon 2020 Framework Program H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement no. 739508, project CAMART². We express our gratitude to Kristine Lazdovica for thermal decomposition temperature measurements and IR property determination, Zane Abelniece and Rolands Capars for conducting the elemental analysis, Vitalijs Rjabovs for assistance with NOESY spectra acquisition, and Lauma Laipniece for HPLC and MS analysis.

REFERENCES

- (1) Ashkin, A. Optical trapping and manipulation of neutral particles using lasers. *Proc. Natl. Acad. Sci. U. S. A.* **1997**, *94*, 4853–4860.
- (2) Grivas, C. Optically pumped planar waveguide lasers: Part II: Gain media, laser systems, and applications. *Prog. Quantum Electron.* **2016**, *45–46*, 3–160.
- (3) Samuel, D. W. I.; Turnbull, G. A. Organic Semiconductor Lasers. *Chem. Rev.* **2007**, *107*, 1272–1295.
- (4) Hung, L. S.; Chen, C. H. Recent progress on molecular organic electroluminescent materials and devices. *Mater. Sci. Eng., R* **2002**, *39*, 143–222.
- (5) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. Electroluminescence of doped organic thin-films. *J. Appl. Phys.* **1989**, *65*, 3610–3616.

- (6) Kozlov, V. G.; Bulovic, V.; Burrows, P. E.; Forrest, S. R. Laser action in organic semiconductor waveguide and double-heterostructure devices. *Nature* **1997**, *389*, 362–364.

- (7) Kozlov, V. G.; Bulovic, V.; Burrows, P. E.; Baldo, M.; Khalif, V. B.; Parthasarathy, G.; Forrest, S. R.; You, Y.; Thompson, M. E. Study of lasing action based on Forster energy transfer in optically pumped organic semiconductor thin films. *J. Appl. Phys.* **1998**, *84*, 4096–4108.

- (8) Zhang, Y.; Forrest, S. R. Existence of continuous-wave threshold for organic semiconductor lasers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 1–4.

- (9) Vembris, A.; Zarins, E.; Kokars, V. Stimulated emission and optical properties of pyranlyden fragment containing compounds in PVK matrix. *Opt. Laser Technol.* **2017**, *95*, 74–80.

- (10) Zarins, E.; Siltane, K.; Pervenecka, J.; Vembris, A.; Kokars, V. Glass-forming derivatives of 2-cyano-2-(4H-pyran-4-ylidene) acetate for light-amplification systems. *Dyes Pigm.* **2019**, *163*, 62–70.

- (11) Guo, Z.; Zhu, W.; Tian, H. Dicyanomehtylene-4H-pyran chromophores for OLED emitters, logic gates and optical chemosensors. *Chem. Commun.* **2012**, *48*, 6073–6084.

- (12) Kato, H.; Ogawa, T.; Ohta, M. Non-benzenoid Aromatic Heterocycles. III. Conversion of 4-Pyrone Derivatives into 4-Pyridone Derivatives. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1468–1469.

- (13) Leblois, D.; Piessard, S.; Le Baut, G.; Kumar, P.; Brion, J.-D.; Sparfel, L.; Sanchez, R.-Y.; Juge, M.; Petit, J.-Y.; Welin, L. Pyrophthalones VII. Synthèse et activité anti-inflammatoire de (pyridinyl-4)-2-indanediones-1,3 substituées sur le noyau benzenique et/ou sur l’hétérocycle. *Eur. J. Med. Chem.* **1987**, *22*, 229–238.

- (14) Peng, Q.; Kang, E. T.; Neoh, K. G.; Xiao, D.; Zou, D. Conjugated alternating copolymers of fluorene and 2-pyridine-4-ylidenemalononitrile: synthesis, characterization and electroluminescent properties. *J. Mater. Chem.* **2006**, *16*, 376–383.

- (15) Shin, M.-S.; Lee, S.-J.; Chin, S.-M.; Lee, S.-H.; Pore, D.M.; Park, Y.-K.; Lee, S.-G.; Hwang, K.-J. Synthesis of Novel Fluorophores Derived from Pyranlydenemalonitrile. *Bull. Korean Chem. Soc.* **2011**, *32* (8), 3152–3154.

- (16) Ha, K.; Heo, J.; Kim, H. J. 2-(1-Propyl-2,6-distyryl-1,4-dihydropyridin-4-ylidene)malononitrile. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2009**, *E65*, o3131.

- (17) Kim, Y. H.; Kim, H. J.; Otgonbaatar, E.; Kwak, C.-H. 2-(2-Methyl-6-phenyl-1-propyl-1,4-dihydropyridin-4-ylidene)propane-dinitrile. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *E67*, o670.

- (18) Lei, Y.; Zhou, Y.; Qian, L.; Wang, Y.; Liu, M.; Huang, X.; Wu, G.; Wu, H.; Ding, J.; Cheng, Y. Polymorphism and mechanochromism of N-alkylated 1,4-dihydropyridine derivatives containing different electron-withdrawing end groups. *J. Mater. Chem. C* **2017**, *5*, 5183–5192.

- (19) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. Enhanced Emission and Its Switching in Fluorescent Organic Nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 14410–14415.

- (20) Lei, Y.; Liu, Y.; Guo, Y.; Chen, J.; Huang, X.; Gao, W.; Qian, L.; Wu, H.; Liu, M.; Cheng, Y. Multi-Stimulus-Responsive Fluorescent Properties of Donor- π Acceptor Indene-1,3-dionemethylene-1,4-dihydropyridine Derivatives. *J. Phys. Chem. C* **2015**, *119* (40), 23138–23148.

- (21) Lei, Y.; Yang, D.; Hua, H.; Dai, C.; Wang, L.; Liu, M.; Huang, X.; Guo, Y.; Cheng, Y.; Wu, H. Piezochromism, acidochromism, solvent-induced emission changes and cell imaging of D- π -A 1,4-dihydropyridine derivatives with aggregation-induced emission properties. *Dyes Pigm.* **2016**, *133*, 261–272.

- (22) Wang, M.; Qian, L.; Guo, Y.; Wu, H.; Liu, M.; Gao, W.; Li, G.; Ding, J.; Huang, X. Solid-state acidochromic properties of barbituric acid-based 1,4-dihydropyridine derivatives with multiple coloured emissions switching. *Dyes Pigm.* **2019**, *160*, 378–385.

- (23) Huang, X.; Zhou, Y.; Qian, L.; Liu, M.; Cheng, Y.; Wu, H. Effective structural modification of traditional fluorophores to obtain organic mechanofluorochromic molecules. *J. Mater. Chem. C* **2018**, *6*, 5075–5096.

- (24) Vembris, A.; Zarins, E.; Jubels, J.; Kokars, V.; Muzikante, I.; Miasojedovas, A.; Jursenas, S. Thermal and optical properties of red

luminescent glass forming symmetric and non symmetric styryl-4H-pyran-4-ylidene fragment containing derivatives. *Opt. Mater.* **2012**, *34*, 1501–1506.

(25) Würthner, F.; Sens, R.; Etzbach, K.-H.; Seybold, G. Design, Synthesis, and Evaluation of a Dye Library: Glass-Forming and Solid-State Luminescent Merocyanines for Functional Materials. *Angew. Chem., Int. Ed.* **1999**, *38* (11), 1649–1652.

(26) Rösch, U.; Yao, S.; Wortmann, R.; Würthner, F. Fluorescent H-Aggregates of Merocyanine Dyes. *Angew. Chem., Int. Ed.* **2006**, *45*, 7026–7030.

(27) Vembris, A.; Muzikante, I.; Gulbinas, V.; Karpicz, R.; Sliuzys, G.; Miasojedovas, A.; Jursenas, S. Fluorescence and amplified spontaneous emission properties of glass forming styryl-4H-pyran-4-ylidene fragment containing derivatives. *J. Lumin.* **2012**, *132* (9), 2421–2426.

(28) Zarins, E.; Puciriuss, T.; Pervenecka, J.; Vembris, A.; Kokars, V. Glass-forming nonsymmetric DWK-dyes with 5,5,5-triphenylpentyl and piparazine moieties for light-amplification studies. *J. Photonics Energy* **2018**, *8* (4), 1–11.

(29) Zarins, E.; Pervenecka, J.; Vembris, A.; Kokars, V. Glass-forming non-symmetric bis-styryl-DWK-type dyes for infra-red radiation amplification systems. *Opt. Mater.* **2019**, *93*, 85–92.

(30) Deshpande, A. V.; Beidoun, A.; Penzkofer, A.; Wagenblast, G. Absorption and emission spectroscopic investigation of cyanovinylidethylaniline dye vapors. *Chem. Phys.* **1990**, *142*, 123–131.

(31) Obuchi, K.; Komatsu, M.; Minami, K. High Performance Optical Materials Cyclo Olefin Polymer ZEONEX. *Proc. SPIE* **2007**, *6671*, 66711I.

(32) Vembris, A.; Zarins, E.; Kokars, V. Solid state solvation effect and reduced amplified spontaneous emission threshold value of glass forming DCM derivative in PMMA films. *J. Lumin.* **2015**, *158*, 441–446.

(33) Würthner, F. Aggregation-Induced Emission (AIE): A Historical Perspective. *Angew. Chem., Int. Ed.* **2020**, *59*, 14192.

(34) Hoche, J.; Schulz, A.; Dietrich, L. M.; Humeniuk, A.; Stolte, M.; Schmidt, D.; Brixner, T.; Würthner, F.; Mitric, R. The origin of the solvent dependence of fluorescence quantum yields in dipolar merocyanine dyes. *Chem. Sci.* **2019**, *10*, 11013–11022.

(35) Wiley, R. H.; Jarboe, C. H.; Ellert, H. G. 2-Pyrones. XV. Substituted 3-Cinnamoyl-4-hydroxy-6-methyl-2-pyrones from Dehydroacetic Acid. *J. Am. Chem. Soc.* **1955**, *77*, 5102–5105.

(36) Bepalov, B. P.; Abolin, A. G.; Romyantsev, V. G. Reaction of γ -pyrones with 1,3-bis(dicyanomethylene)indan. *Chem. Heterocycl. Compd.* **1985**, *21*, 501–506.

(37) Siram, R. B. K.; Tandy, K.; Horecha, M.; Formanek, P.; Stamm, M.; Gevorgyan, S.; Krebs, F. C.; Kiriya, A.; Meredith, P.; Burn, P. L.; Namdas, E. B.; Patil, S. Synthesis and Self-Assembly of Donor-Acceptor/Donor Based Oligothiophenes and Their Optoelectronic Properties. *J. Phys. Chem. C* **2011**, *115*, 14369–14376.

(38) Wang, S.; Kim, S.-H. New solvatochromic merocyanine dyes based on Barbituric acid and Meldrum's acid. *Dyes Pigm.* **2009**, *80*, 314–320.

(39) Andreu, R.; Franco, S.; Galán, E.; Garín, J.; de Baroja, N. M.; Momblona, C.; Orduna, J.; Alicante, R.; Villacampa, B. Isophorone- and pyran-containing NLO-chromophores: a comparative study. *Tetrahedron Lett.* **2010**, *51*, 3662–3665.

(40) Andreu, R.; Carrasquer, L.; Garín, J.; Modrego, M. J.; Orduna, J.; Alicante, R.; Villacampa, B.; Allain, M. New one- and two- dimensional 4H-Pyranylidene NLO-phores. *Tetrahedron Lett.* **2009**, *50*, 2920–2924.